

ALLEN COUNTY PUBLIC LIBRARY



3 1833 01888 4004

GC

929.1

F221GR,

V.2

Great Chemists

In two volumes

Volume 2

Great Chemists

Edited by Eduard Farber

In two Volumes

Volume

2

Interscience Publishers · New York · London

1961

Copyright © 1961 by Interscience Publishers, Inc.
ALL RIGHTS RESERVED
Library of Congress Catalog Card Number 60-16809

Printed in the United States of America

Acknowledgments

This book could not have been produced without the cooperation of the authors of the individual biographies, nor without the gracious help of many publishers and authors who kindly consented to reproduction or translation of biographies published previously, and the Editor hereby extends to them, as well as to the authors of the original biographies, his gratitude. Further detailed credit is given at the end of each biography; here we can mention briefly: Verlag Chemie; Springer Verlag; Taylor & Francis, Ltd.; Gazzetta Chimica Italiana; The Washington Academy of Sciences; American Pharmaceutical Association; *American Dyestuff Reporter*; American Chemical Society (*Journal of Chemical Education*; JACS); The Smithsonian Institution; University of Pennsylvania Press; The Royal Society (London); Society of the Chemical Industry; *Nature*; National Academy of Sciences (U.S.); Société Chimique de France; The Chemical Society (London); American Institute of Mining, Metallurgical and Petroleum Engineers; University Press, Cambridge; Princeton University Press; New York Academy of Science; Nobel Foundation; Yale University Press; American Institute for the History of Pharmacy; American Association for the Advancement of Science (*Science and Scientific Monthly*); University of Chicago Press; Salmon (Paris); University of Wisconsin Press; USSR Academy of Science; Oxford Bibliographical Society; *Naturwissenschaften*; The Cavendish Society; *American Journal of Science*, the Royal Swedish Academy of Science, and Akademie-Verlag.

In addition, grateful acknowledgment is hereby made to those who supplied many of the illustrations used in this book: Mrs. Dorothea H. Williams, Custodian of the Smith Collection, Philadelphia, for her invaluable help; The University Museum, Philadelphia, for the illustrations on pg. 2; Istituto Nazionale Medico Farmacologico, Rome, pp. 42 and 44; The Smithsonian Institution, pp. 48, 202, 536, 832, 854, 960, 1014, 1086, 1120, 1146, 1204, and 1264; The Library of Congress, pp. 66, 150, 178, and 284; Bettmann Archive, pg. 82; Duveen Historical Library, pp. 228, 240, 254, and 264; Academic Press, pp. 326, 750, 1326, 1334, and 1344; *J. Chem. Ed.*, pp. 704, 1376, 1422, and 1470; Mrs. James B. Conant, pg. 806 (Richards); University of Wisconsin, pg. 806 (Babcock); Mrs. Harvey W. Wiley, pg. 806 (Wiley); Alexander Silverman, University of Pittsburgh, pg.

908; La Wall and Harrison, Philadelphia, pg. 926; Deutsches Museum München, pg. 982; Professor Terje Enkvist, Helsinki, pg. 1112; *Endeavor*, pp. 1158 and 1454; *Cornell Chemist*, pg. 1182; Arthur D. Little, Inc., pg. 1192; The Dow Chemical Company, pg. 1220; Verlag Chemie, pp. 1300, 1366, and 1442; Dr. Robert Tiffeneau, Paris, pg. 1390; Professor Janick Bjerrum, Copenhagen, pg. 1490; Österreichische Nationalbibliothek, Bild-Archiv and Porträt-Sammlung, Wien, pg. 1552; Massachusetts Institute of Technology, pg. 8.

Contents

Volume 2

- 60 Victor Meyer By *R. Meyer, translated by E. Farber* 853
- 61 Johan Peter Klason By *S. Nauckhoff, translated by Julia C. Molander* 865
- 62 Henry Edward Armstrong By *H. Hartley* 875
- 63 Henry Le Chatelier By *A. Silvermann* 907
- 64 Herman Frash By *W. Haynes* 921
- 65 Interlude IV, Scientists and Industrialists By *E. Farber* 935
- 66 Jacobus Henricus van't Hoff By *E. Cohen, translated by Ralph E. Oesper* 947
- 67 Henri Moissan By *A. Stock, translated by Ralph E. Oesper* 959
- 68 Emil Fischer By *B. Helferich* 981
- 69 Sir William Ramsay By *C. Moureu* 997
- 70 Otto Nikolaus Witt By *E. Noelting, translated by E. Farber* 1013
- 71 Wilhelm Ostwald By *E. Farber* 1019
- 72 Albrecht Kossel By *K. Felix, translated by E. Farber* 1031
- 73 Paul Ehrlich By *R. Koch, translated by Ralph E. Oesper* 1039
- 74 Arthur Rudolf Hantzsch By *A. Weissberger* 1065
- 75 Giacomo Ciamician By *R. Fabre, translated by E. Farber* 1085
- 76 Svante Arrhenius By *W. Palmaer, translated by Ralph E. Oesper* 1093
- 77 Ossian Aschan By *W. Hückel, translated by E. Farber* 1111

- 78 Philippe-Auguste Guye By E. Briner, translated by E. Farber 1119
- 79 John Ulric Nef By M. L. Wolfrom 1129
- 80 Charles Moureu By C. Dufraisse, translated by E. Farber 1145
- 81 Frederic Stanley Kipping By F. Challenger 1157
- 82 Leo Hendrik Baekeland By W. Haynes 1181
- 83 Arthur Dehon Little By W. Haynes 1191
- 84 Walther Nernst By A. Einstein 1203
- 85 Moses Gomberg By C. S. Schoeppfle and W. Bachmann 1209
- 86 Herbert Henry Dow By W. Haynes 1219
- 87 Alfred Werner By P. Pfeiffer, translated by Ralph E. Oesper 1233
- 88 Wilder Dwight Bancroft By A. Findlay 1245
- 89 Marie Curie By F. C. Wood 1263
- 90 Vladimir N. Ipatieff By C. B. and H. E. Marquand 1277
- 91 Fritz Haber By K. F. Bonhoeffer, translated by Ralph E. Oesper 1299
- 92 Phoebus Aaron Theodor Levene By M. L. Wolfrom 1313
- 93 Fritz Pregl By H. Lieb, translated by E. Farber 1325
- 94 Victor Grignard By C. Courtois, translated by E. Farber 1333
- 95 Lord Rutherford By A. S. Eve and J. Chadwick 1343
- 96 Richard Willstätter By E. Farber 1365
- 97 Nevil Vincent Sidgwick By H. T. Tizard 1375
- 98 Marc Tiffeneau By E. Fourneau, translated by E. Farber 1389
- 99 Carl Bosch By A. Holderman, translated by Elisabeth F. Lanzl 1397
- 100 John Edgar Teeple By W. Haynes 1409
- 101 Alfred Stock By E. Wiborg, translated by E. Farber 1421
- 102 Franz Fischer By H. Koch, translated by E. Farber 1433

CONTENTS

103	Heinrich Wieland	By <i>E. Farber</i>	1441
104	Francis William Aston	By <i>G. P. Thomson</i>	1453
105	Frederick Soddy	By <i>A. S. Russell</i>	1463
106	Johannes Nicolaus Brønstead	By <i>R. P. Bell</i>	1469
107	Niels Janniksen Bjerrum	By <i>E. A. Guggenheim</i>	1489
108	Irving Langmuir	By <i>K. H. Kingdon</i>	1507
109	Hans Fischer	By <i>H. Wieland</i> , translated by <i>Ralph E. Oesper</i>	1525
110	Claude Silbert Hudson	By <i>M. L. Wolfson</i>	1535
111	Ernst Späth	By <i>A. A. Bacher</i>	1551
112	Victor Moritz Goldschmidt	By <i>P. Rosbaud</i>	1563
113	Thomas Midgley, Jr	By <i>W. Haynes</i>	1587
114	Wallace Hume Carothers	By <i>R. Adams</i>	1599
	Epilogue		1613
	Index		1619

Volume 1

- 1 Babylonian Chemists By M. Levey 1
- 2 Interlude I, Philosophers and Practitioners By E. Farber 7
- 3 Arabic Chemists By M. Levey 13
- 4 Interlude II, Philosophical Alchemists and Practical Metallurgists By E. Farber 39
- 5 Paracelsus By R. P. Multhauf 47
- 6 Libavius and Beguin By R. P. Multhauf 65
- 7 Joan Baptista Van Helmont By J. R. Partington 81
- 8 Rudolph Glauber By Paul Walden, translated by Ralph E. Oesper 115
- 9 Robert Boyle By Marie Boas Hall 135
- 10 Nicolas Lemery By B. Fontenelle, translated by R. P. Multhauf 149
- 11 Herman Boerhaave By M. Kerker 163
- 12 Duhamel du Monceau By Felix Vicq-d'Azyr, translated by E. Farber 177
- 13 Guillaume-François Rouelle By C. Secrétan, translated by E. Farber 185
- 14 Andreas Sigismund Marggraf By E. O. von Lippmann, translated by E. Farber 193
- 15 Mikhail Vasil'evich Lomonosov By H. M. Leicester 201
- 16 Joseph Black By Henry, Lord Brougham 211
- 17 Henry Cavendish By G. Cuvier, translated by E. Farber 227
- 18 Joseph Priestley By William Henry 239
- 19 Carl Wilhelm Scheele By D. L. Crell, translated by E. Farber 253
- 20 Antoine Laurent Lavoisier By D. I. Duveen 263
- 21 Interlude III, The Chemists' Language By E. Farber 283
- 22 Martin Klaproth By G. Bugge, translated by Ralph E. Oesper 293

CONTENTS

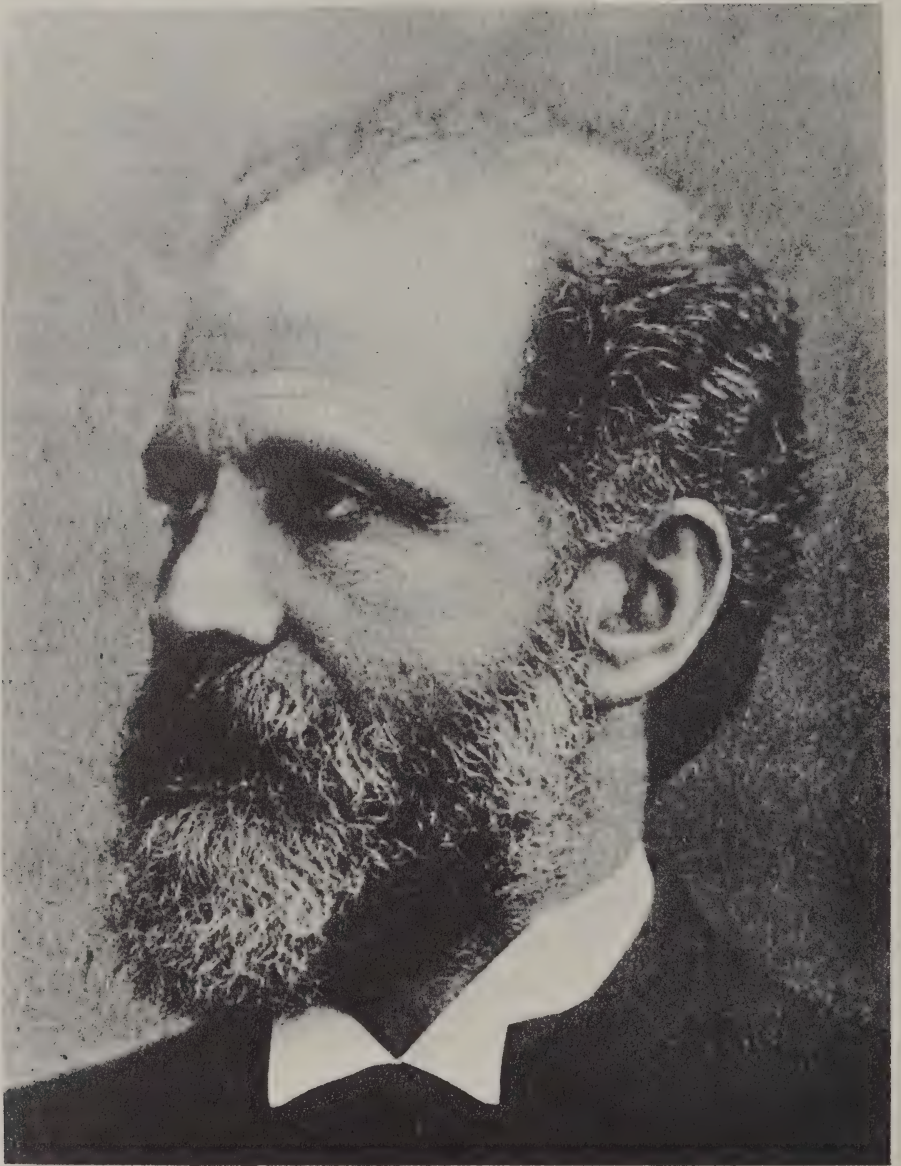
- 23 Benjamin Rush By W. D. Miles 303
- 24 Claude-Louis Berthollet By E. Farber, translated by Dora S. Farber 315
- 25 Joseph Louis Proust By E. Farber, translated by Dora S. Farber 325
- 26 John Dalton By A. Hopwood 333
- 27 Louis Jacques Thenard By P. Flourens, translated by C. A. Alexander 343
- 28 Gay-Lussac By F. Arago, translated by E. Farber 359
- 29 Humphry Davy By R. Siegfried 369
- 30 Jöns Jacob Berzelius By A. J. Ihde 385
- 31 Benjamin Silliman By W. D. Miles 403
- 32 Robert Hare By W. D. Miles 419
- 33 Michel-Eugène Chevreul By M. E. Weeks and L. O. Amberg 435
- 34 Leopold Gmelin By E. Pietsch and E. Beyer, translated by Dora S. Farber 453
- 35 Michael Faraday By A. J. Ihde 465
- 36 Eilhardt Mitscherlich By G. Rose 481
- 37 Anselme Payen By M. Phillips 495
- 38 Friedrich Wöhler By A. von Hoffman, translated by Elizabeth F. Lanzl 505
- 39 Jean-Baptiste Dumas and Charles-Adolphe Wurtz By G. Urbain, translated by E. Farber 521
- 40 Justus von Liebig By F. Haber, translated by Dora S. Farber 535
- 41 Thomas Graham By W. Odling 551
- 42 Robert Wilhelm Bunsen By T. Curtius, translated by E. Farber 573
- 43 Hermann Kopp By T. E. Thorpe 583
- 44 Henri Sainte-Claire Deville By R. E. Oesper and P. Lemay 601

- 45 August Wilhelm von Hofmann By *B. Letsius, translated by Ralph E. Oesper* 625
- 46 Louis Pasteur By *R. Koch, translated by Ralph E. Oesper* 641
- 47 Stanislao Cannizzaro By *D. Marotta, translated by Alfred A. Bacher* 661
- 48 Marcelin Berthelot By *E. Farber, translated by Dora S. Farber* 675
- 49 Alexander Mikhaïlovich Butlerov By *H. M. Leicester* 687
- 50 August Kekulé By *R. Anschütz, translated by E. Farber* 697
- 51 Archibald Scott Couper By *O. T. Benfey* 703
- 52 Dmitrii Ivanovich Mendeleev By *H. M. Leicester* 717
- 53 Adolf von Baeyer By *R. Willstätter, translated by Ralph E. Oesper* 733
- 54 Johannes Diderik van der Waals By *H. Kamerlingh Onnes* 749
- 55 Sir William Henry Perkin By *S. M. Edelstein* 757
- 56 Ernest Solvay By *R. Étienne, translated by E. Farber* 773
- 57 Josiah Willard Gibbs By *C. A. Kraus* 783
- 58 American Chemists at the Turn of the Century: S. M. Babcock, Harvey Wiley, Ira Remsen, T. W. Richards, and Edgar Fahs Smith By *A. J. Ihde* 805
- 59 Otto Wallach By *L. Ruzicka* 831

.. 60 ..

Victor Meyer

1848-1897



VICTOR was born September 8, 1848, in Berlin. Our father, Jacques Meyer, had come to Berlin from Hohensalza as a very young man. He gradually developed a cotton business which grew into a calico printing and dyeing plant. Although our father had no chemical or technical training he was an avid reader of Dingler's Polytechnical Journal. He was married in 1845. Of the four children Victor was the second, I the eldest.

Victor and I received our first instruction from our mother. In 1858 we entered the gymnasium. He was convinced that he would become an actor. Even after graduating in 1865 he was little inclined to follow our father's wish and study chemistry. Then he visited me when I was studying chemistry in Heidelberg, and suddenly arrived at a decision. Bunsen became his ideal—and remained so to the end of his life.

Victor spent his first semester in Berlin and attended A. W. Hoffmann's lectures, returning to Heidelberg to live with me. When I left there in the spring of 1866 he remained to continue his studies. On May 13, 1867, he obtained the degree of Doctor of Philosophy, *summa cum laude*, not quite nineteen years old and just beginning his fifth semester. From the government Bunsen had received a continuing order to analyze the mineral waters of Baden, and a special assistant had been granted to him for this work. He offered the assistantship to the young doctor; Victor accepted it and, therefore, remained in Heidelberg for another year.

IN BAEYER'S LABORATORY, 1868-1871

At the end of the summer term of 1868, my brother left Heidelberg and returned to Berlin to study in Adolf Baeyer's laboratory. The three years he spent in this atmosphere were decisive for his future. The series of his publications began with a notice about trimethyl-glyceryl-ammonium, an analog to "neurine." The discovery of a way to synthesize aromatic acids with sodium formiate

brought him into close contact with the most pressing questions of benzene chemistry.

STUTTGART, 1871-72

In 1871 he went from Berlin to Stuttgart as associate professor, a position which he described in a letter as "outright paradisiacal." One day he noticed in his audience an elderly stout gentleman who followed the lecture with greatest attention. It was Carl Kappeler, president of the Swiss Board of Education, who alone was responsible for filling the professorships at the Zurich Polytechnicum. After the lecture he had a long conversation with Victor; Kappeler told him that he would like to offer him a professorship but hesitated because he was too young for it. When Victor replied that this fault would be diminished from day to day, the old gentleman smilingly agreed, and it was not long before Victor became full professor of general chemistry in Zurich, after scarcely one year in Stuttgart.

ZURICH, 1872-1885

In the beginning Victor's activities in Zurich were anything but successful; he was bitterly disappointed by his initial reception. In a letter of March 2, 1873, he was very caustic about it. "I have brought down another assistant from Stuttgart so that I now have two unconditionally devoted assistants who should be able to oppose the intrigues of the Swiss. I can say, without superciliousness, that I have almost been deified by my Stuttgart students, they loved me far beyond my merits, whereas here I find only enmity and suspicion. . . ." Later on, after his marriage in March, 1873, the situation changed completely.

The year 1872 brought the discovery of the aliphatic nitro compounds. In the great field opened by this discovery Victor and a number of his students determined the constitution and the course of their many reactions. His interest was particularly aroused by the unexpected acidity of the primary and secondary nitroparaffins and by the reactions with nitrous acid. He explained the acidic function as an influence of the negative nitro group on the hydrogen atoms connected with the same carbon atom. Later

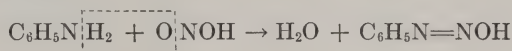
on this explanation was replaced by a different one, based on a desmotropic rearrangement taking place when the nitroparaffins form salts:



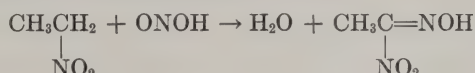
so that they are to be considered pseudo-acids in the nomenclature of Hantzsch.

Victor compared the reaction of nitrous acid upon primary and secondary nitro compounds with the reaction of this acid on primary and secondary aromatic amines, giving diazo compounds from the first and nitrosamines from the second. This leads to the formulas of nitrolic acids and pseudo-nitrols which Victor expressed in the following way:

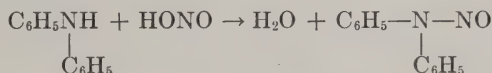
Primary Aromatic Amine.



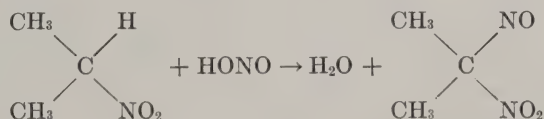
Primary Aliphatic Nitro Compound (Nitrolic Acid).



Secondary Aromatic Amine.



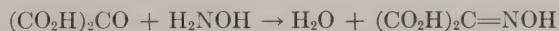
Secondary Aliphatic Nitro Compound. (Pseudo-Nitrol).



The nitrolic acids thus appear to be derivatives of hydroxylamine $\text{H}_2\text{N.OH}$. If this were correct, then the reaction of nitrous acid



with malonic acid should yield an oximido body, the same as obtainable from hydroxylamine and mesoxalic acid:



This was actually found to be true (1883).

The year 1882 saw the start of a great new series of studies as a result of the discovery of thiophen. In the introduction to his book on thiophen (Braunschweig, Vieweg & Sohn, 1888) Victor wrote:

The first stimulus to the experiments on the isolation of thiophen I owe to an accident. In an experiment during a lecture I wanted to demonstrate to my audience the reaction by which benzene can be identified. The basis of this identification is that benzene, or rather, as we have to say now, thiophen-containing coal tar benzene, produces the deep-blue indophenine when treated with isatin and concentrated sulfuric acid. Immediately before the lecture I made sure that the reaction takes place, and I was greatly surprised to obtain a complete blank when I tried to use this phenomenon in the lecture itself for the purpose of characterizing as benzene the oil produced by distilling benzoic acid with lime. My assistant at that time was T. Sandmeyer, the discoverer of many reactions of which only a few are named after him; he immediately brought it to my attention that the test before the lecture had been made with a different sample of benzene, and with this sample the experiment proceeded readily as desired. The riddle was, however, not solved by this demonstration; I stated this surprising phenomenon to my audience right there and added the remark that a problem existed here which should yield important information through experimental work.

Experiments were begun the same day, and they indicated how the matter was to be pursued. It was found that the purest samples of benzene from coal tar invariably gave the blue color reaction, and that this could be eliminated by extracting or warming the benzene with sulfuric acid. When the sulfo acid obtained by the treatment with sulfuric acid was distilled, an "active" benzene was formed which again showed a positive indophenin reaction.

Three hypotheses were tried in an effort to explain these reactions: (1) Benzene itself is indifferent towards isatin and sulfuric acid; the product from coal tar, however, contains a small impurity which catalyzes benzene so that it reacts. (2) On the other hand, benzene produced from benzoic acid could contain an impurity which cancels the reaction. (3) Benzene from coal tar

could be a mixture of two substances, very similar physically and chemically, although one is more reactive than the other; the more reactive one would combine with isatin and be the first to form a sulfo acid in the treatment with sulfuric acid.

The third of these hypotheses proved correct. The isolation of the "more reactive substance" was achieved through its quicker sulfonation reaction. Victor's thiophen book listed more than one hundred papers published by him with a large number of students during the years 1882 to 1887.

On July 13, 1884, Hans Hübner (born 1837) in Göttingen died suddenly of a heart attack, and Victor was proposed as his successor. At that time, his health was poor. In the spring he had had an attack of kidney stones, followed by a neuralgia which became almost unbearable during the summer. The pain markedly depressed his spirits. On October 23, 1884, he wrote about "the hundreds of people who reproach me for intending to leave Zurich . . ." and on October 26: ". . . I assure you that I am the least enviable man in the world, and that with all my outwardly successes and apparent glamor I have time and again wished with all my heart I were a poor artisan but had my health back."

GÖTTINGEN, 1885-1889

Victor arrived in Göttingen on April 23, 1885. He was surrounded by a staff of very able assistants, and work started immediately. Thiophen was still in the foreground. Experiments on vapor densities, which he had started in 1876, were suspended temporarily; a pyrochemical room still had to be built. In the summer of 1886 the number of students in the laboratory was 105 as "against 59 last summer. Even in the best time under Wöhler such a large number had never been reached."

During the lecture on February 4, 1888, there was a violent explosion. "I wish to inform you, in case it should be reported in the newspapers (which I don't hope) that nobody was hurt. The destruction in the lecture room, however, was tremendous. A mixture of air and carbon disulfide had ignited. I am now reading experimental chemistry for the eighteenth time, and yet every year

something new happens that one did not know. By the way, how do you like my lecture-experiment on nitrogen chloride? . . . Very often, it has exploded under our hands without harming us, since we were protected. This is one of the most interesting and exciting studies I have ever undertaken."

This way of working was characteristic of Victor. Danger attracted him, whether in the high mountains or at the laboratory bench, but he did not expose himself to it blindly, he met it with the tools of informed prudence. Experimenting was his element, and the lecture on experimental chemistry always was his greatest joy. At that, he was not even especially skillful with his hands, but he had an inventive head, untiring in planning new methods.

The new laboratory building was completed and the dedication ceremony was set for November 15, 1888. At that time something extraordinary happened; its dramatic course is best described in Victor's own words from his letters:

November 11: Strictly confidential! Yesterday I received a highly complimentary official invitation from the Baden Ministry to the chair of Bunsen in Heidelberg. Form and content of the letter are outright fabulous; I have to blush when I read it. . . . Yet this Thursday the new Institute is to be solemnly dedicated. . . . What shall I do in my unhappy state ("ich Unglücksmensch").

November 28: This is a bitter day: I have just declined Heidelberg—in the same hour I receive a telegram that the ground adjacent to Bunsen's laboratory has almost been bought, where I was to build an organic laboratory. Naturally, my resolution is firm and unchangeable, and I don't want to repent it.

December 1: We are taking this matter terribly seriously, and it will be a long time before the wound ceases to bleed.

March 24, 1889: After spending all winter in a feverish excitement about Heidelberg, a second call really arrived . . . it is and remains ungrateful to the Prussian ministry that has done so much for me, and I did not sign but declined for the second time.

Whereupon Emil Fischer received the call to Heidelberg and declined. In the meantime Bunsen had written to the Prussian Ministry, requesting that Victor be released to become his successor, and now Victor finally accepted.

HEIDELBERG, 1889-1897

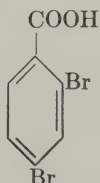
In a letter dated October 2, 1889, Victor announced his arrival in Heidelberg. "Everything is beautiful and magnificent, but still much disorder and much to be done."

On January 28, 1890, he gave a lecture in Berlin on "Results and aims of stereochemical research." He had introduced the name "stereochemistry" two years before.

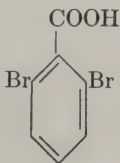
About his work Victor wrote on December 11, 1891:

In the laboratory I am feeling quite well, thank God, I have a large number of very interesting projects. . . . Thus I am assiduously working on the action of CO_2 on H_2 , and I am obtaining quite different results from those of previous observers, the same in the combustion of fulminating gas ($\text{O}_2 + \text{H}_2$). . . . I have such convenient methods now that it is a pleasure to use them. Furthermore I have obtained astounding results in the reaction of chlorine and bromine on the very simplest organic compounds. . . . My nerves are behaving quite a lot better since the start of the semester. It is now one week that we have here the first female student.

On April 29, 1894, he wrote to Baeyer about his first observations which led him to the finding of steric hindrances in chemical reactions: "It is strange that substituted benzoic acids which have substituents to the right and left of COOH are scarcely or not at all esterified by alcohol and hydrochloric acid. The causes are steric and permit a kind of comparative measurement of the size of atoms and radicals.



yields about 95 per cent ester,



yields no ester at all. Methyl acts less repellent than bromine."

Among the groups which prevent esterification when present on both sides of a carboxyl is carboxyl itself. Now the question arose whether the twice ortho-substituted carboxylic acids cannot be esterified at all, or whether this occurs only in the reaction with alcohol and hydrochloric acid. The answer resulted from the action of methyl iodide on the silver salts of the acids; the methyl esters were obtained in almost quantitative yields.

The influential size of the substituents in the stereochemical sense is not the same as Kopp's "relative volumes." Stereochemically, methyl and ethyl act exactly like cetyl, $C_{16}H_{33}$. All the steric action of the long atom chain $CH-CH \dots CH_3$ is exerted only by the first carbon atom in direct bond with the benzene ring.

On July 23, 1895, he wrote to Baeyer: "I have very strongly taken up pyrochemistry again. The other day I built a small oven for vapor-density determinations in which platinum and a 30 per cent iridium-platinum can easily be melted. I should like to measure the density of mercury, iodine, zinc, cadmium and other so-called 'atoms' at 2000 to 3000° C."

At that time he was feeling quite well. However, the summer of 1896 was "one of the worst I ever had," and the beginning of 1897 found him in rather unsatisfactory health. In spite of his illness he was busy with many things, among others the plans for a new large addition to his laboratory building. Thus the summer semester was a very active one for Victor, and he was making plans for a vacation in his beloved Swiss alps.

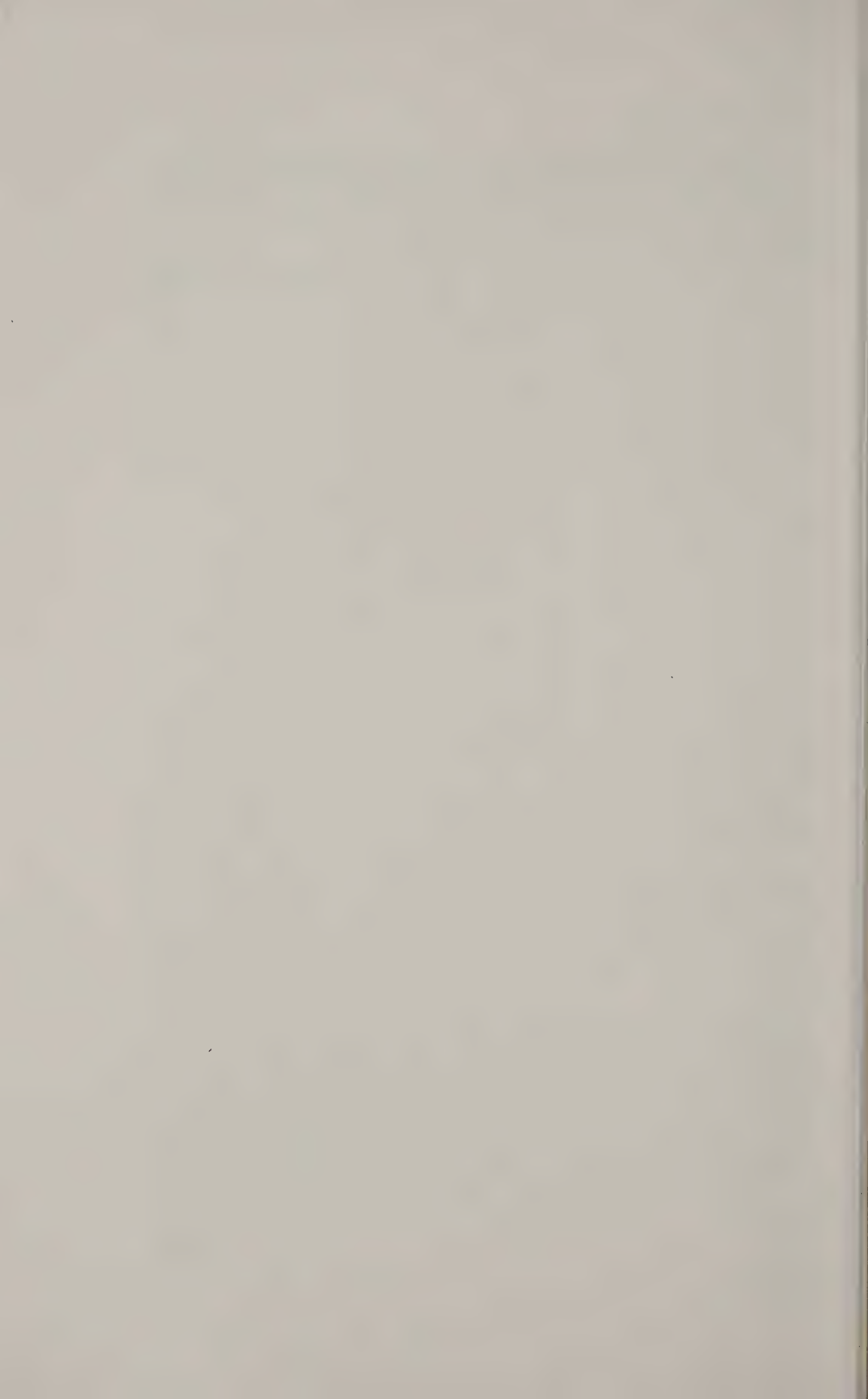
Then, on August 8, like lightning out of a blue sky, came the news of his death. He had ended his life by taking prussic acid. On a small leaflet, we found these few words, written in a fleeting hand: "Beloved wife! Beloved children! Good bye! my nerves are giving out; I cannot go on."

His friend and neighbor Willy Kühne, director of the Physiological Institute, wrote a few days afterwards: "Already 13 years ago Victor was prevented from taking his own life, unfortunately, he could not be hindered in always being prepared to do it. Since that time he had stood up heroically under the neuralgic pains and sleeplessness, and he overcame them by his gigantic work until the fear of mental collapse . . . seized him in a sudden frenzy."

VICTOR MEYER

Selections from the biography by his older brother, Richard Meyer,
in *Berichte der Deutschen Chemischen Gesellschaft*, 41, 4505–
4718 (1908). Translated by Eduard Farber.

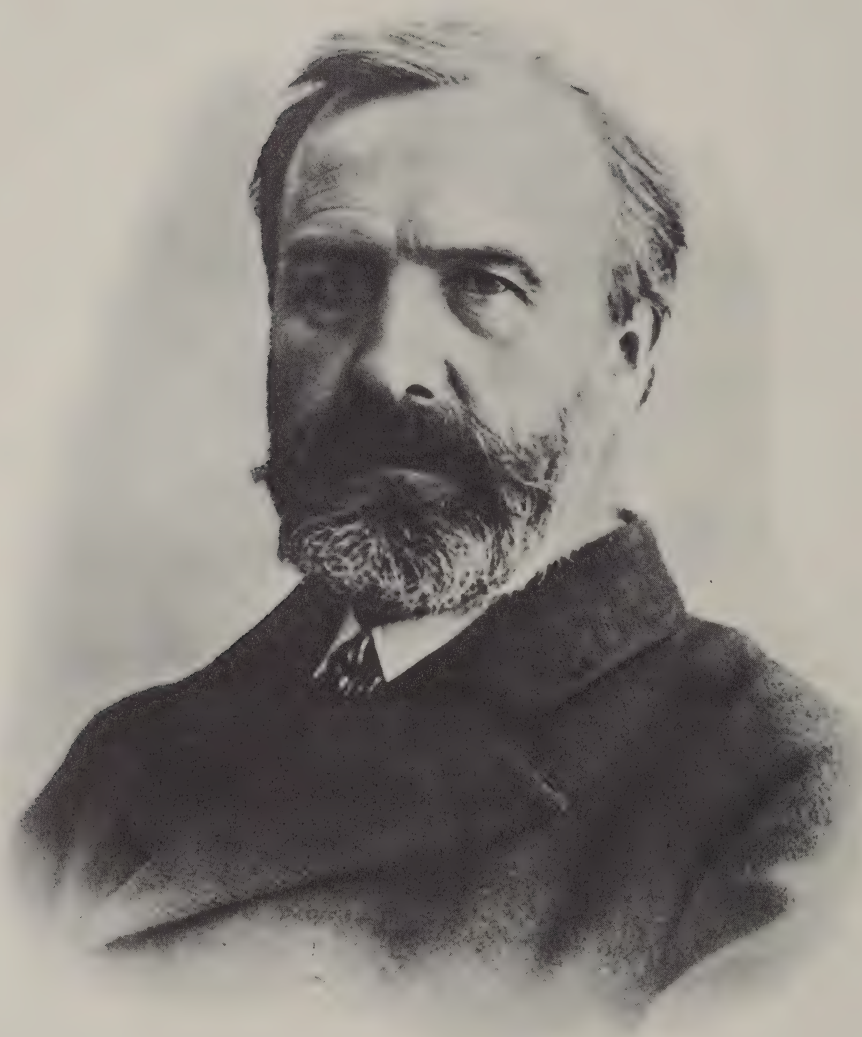
RICHARD MEYER



.. 61 ..

Johan Peter Klason

1848-1937



IN A *Festschrift* which his former students dedicated to their teacher on his sixtieth birthday, Peter Klason published his autobiography. As motif, he used the words from Goethe's *Faust*: "*Es irrt der Mensch so lang er strebt.*" It might be an expression of Peter Klason's conception of himself. During his life as a scientist he often had a feeling of being a Faustian personality—searching and pondering, sometimes doubting himself and the correctness of his theories, his inquiring mind reaching for the goal of his aspiration.

Johan Peter Klason was born on April 4, 1848, the only son of Kristoffer Adam Claesson (1821–1906), manager of the Sannarps estate, later superintendent, and his wife Elsa Helena Claesson, née Billing (1823–1913). His father as well as grandfather and great-grandfather were agricultural superintendents for the property of a landowner of the nobility. They were descendants of a glass blower who had immigrated from Bohemia to Sweden. Klason's father was elected principal of the first agricultural school in Sweden, at Wrangelsro.

His mother was descended from an old family of clergymen in the diocese of Gothenburg. Her maternal grandfather, like her father, had been vestry keepers and "lived," quoting Klason's own words in his autobiography, "a happy existence with music, song, and carousing; besides, he was busy with blood-letting." Peter Klason wrote very little about his parents, but much more about his maternal grandmother and her competence. He was born in the modest cottage of his maternal grandparents near the manor house. Among the many rules his grandmother impressed on him was one which he never forgot: "Beware above all of pride. The deeds of humility are the ones which are everlasting."

At the age of five, Peter went to the mobile grade school which was then situated in his parish, Arstad, but at six he went to the more permanent school at Getinge. When he was nine years old, he started the first class in a school in Halmstad. In his autobiography he tells about the modest conditions in this school, which

he attended until 1863, when he was transferred to a private school in Lund. He passed his maturity examination at the public school in Malmö in 1867.

Klason had not made up his mind about his future career. Therefore, he remained at home for a year. Evidently his intention was to be a farmer, but his desire to study was too strong, and in 1868 he entered Lund university and received a diploma in modern education. He was thinking of taking a course in metallurgy, but was discouraged by his friends' descriptions of the long and hard studies, and the difficulties in obtaining a diploma. After the necessary examinations in Latin, his way was open for studies in the humanistic fields, but he changed to a scientific course. The educational staff in the scientific field at the Lund University was remarkable: for botany, Agardh; for zoology, Sven Nilsson; for geology, Torell; and as teacher in chemistry, Blomstrand, to mention only a few names in the faculty of science.

Blomstrand's teaching chiefly comprised organic chemistry and the analysis of minerals. Klason probably spent most of his time on such subjects in the laboratory, at least during his first year. He also followed Blomstrand on his mineral excursions.

Research of the organic sulfur compounds had become a tradition in Lund. It had its origin with the work of William Christopher Zeise (1789–1847), a Dane, who had begun the experiments and produced ethyl mercaptane in 1833. Even Blomstrand was interested in this research. Following Blomstrand's suggestions, Klason wrote his doctor's thesis "On phenyl- and ethyl-sulfacetic acids and sulfonic acids derived from them" and defended it in 1874. He remained faithful to this topic for many years of his research work at Lund. During his years of study he also spent some time at the laboratories of A. W. Hofmann in Berlin, Kolbe in Leipzig, and others in Germany.

Not until 1887 did he become laboratory professor at the chemical institution with a very small salary. One can understand, therefore, that it was necessary for him to seek additional occupations for some extra income. In 1880 he held a teaching job at the Lund Cathedral School. He was thinking of industrial work and tried to qualify for a position in the recently finished gas works in Lund. For this purpose he spent a few months at the gas

works in Malmo. Although he was not appointed to the position he wanted, he became president of the board of directors for the Lund Gas and Water Works. In this capacity he was in charge of the first effort to create a modern sewer system in Lund. In earlier times this city was completely without sewers; among the inconveniences ought to be mentioned the fact that the evil-smelling refuse from Klason's sulfur research at the laboratory was simply emptied into the gutter; consequently, the smell was detected throughout the whole town.

His position as controller at the Klippans Brewery also helped to better Klason's economic status. This was his first acquaintance with the brewery trade and was of great importance for his future prospects in the brewery association.

Klason at this time had thoughts of getting married; and naturally he wanted a better economical foundation than the academic career had to offer. The object of his tender passion was Marie Louise Hill, daughter of the well-known professor of mathematics, K. J. Hill.

When the professorship in chemical technology at "KTH" (the Chemical Institute of the Technical University in Stockholm) was open after the death of F. L. Ekman, a substitute teacher was appointed, but Professors Otto Pettersson and L. F. Hilsson found Klason a more suitable permanent representative for the post. For his inaugural lecture Klason chose the topic: "About manufacturing illuminating gas." It was then one of the few branches of chemical technology that Klason knew from personal contact. His chemical qualifications were superior to those of his competitors. As a remarkable sign of the times ought to be mentioned that one of his competitors had chosen the subject "The significance of electricity for the chemical technology." The Swede, Oscar Carlson, in 1890 had applied for a patent on a method to make hypochlorites and chlorates by electrochemical means; this later became the foundation for the electrochemical industry.

Klason was appointed professor on August 19, 1890, and also was named principal of the chemical technical school. He was confronted with many obstacles in his new position; the board of administrators needed his assistance. The chemical laboratory was overcrowded, and it was necessary to build a new one. The num-

ber of students had to be increased. The necessity for three or four years of instruction for the chemical technical school was disputed among the teaching staff and the administrators.

Klason once proposed that our universities should create technology departments, including technical botany. Perhaps Klason made this decision because he himself had much interest in botany during his student years. A more cogent reason, however, was that this subject was closely associated with fermentation technology and with wood research, subjects which now interested him to a high degree.

The old laboratories in the south wing of the Technical University had been inadequate, and it was difficult to find room for the study of new subjects. This went so far that the new professor of chemical technology had to give up his apartment in the building, and that the former kitchen of janitor Carlsson had to be used for fermentation studies.

The new building of the technical school was the most important issue during the first ten years of Klason's professorship. I shall not tire the reader by detailing the various difficulties, schemes, and all the different committees with which he had to be in touch before the new building was ready in the fall of 1898.

In Germany Klason had gained many experiences which he used in the laboratory. One could say without exaggeration that it was the most modern and practical laboratory in our country at that time.

The new laboratory building even contained premises for the electrochemical instruction which in Klason's opinion ought to be improved. This subject had been included in the school's curriculum since 1894. At first, the subject was voluntary, but after the faculty had the good fortune to acquire K. W. Palmaer as a teacher, it became compulsory for the students of chemistry in their third-year course. At this time physical chemistry, through Svante Arrhenius' contributions, had broken through the older concepts of chemistry, and it was therefore natural that much of the instruction was in the theoretical part of electrochemistry.

When Klason joined the university, only 80 students were admitted each year. This number increased later to 100, and in 1901 a heated discussion started whether 180 new students ought

to be admitted each year. This question was again discussed in 1908 and a number of 240 new students was proposed by the experts.

During his appointment at the Technical University, Klason had to answer a great many questions of chemical import, and in many other ways he came in contact with numerous chemical industries. I shall only mention here the inquiry into arsenic which was in the daily news at that time, caused by the assumption that the paint used in the offices for certain civil service departments in the old *Riksdags* buildings contained poisons. Another inquiry came from a lawsuit between a Swedish sulfite factory and the mining company that had delivered a sulfide ore which contained selenium.

Klason's greatest passion was research in lignin. He was determined to find the chemical composition of lignin of which all wood contains about 30 per cent. He spent almost forty years, particularly the last twenty-five years of his life, on this problem. His visit at the Delary paper mill during his student years aroused his interest in the research of cellulose. The pine trees interested him above everything else.

In his autobiography, Klason pays his homage to the pine trees of the north and he compares them with the palms of the south. He ends with these words: "The forest is our happiness, our comfort and our wealth."

His first results on this subject were announced in a lecture at the chemical association in 1891. His articles in *Technical Tidskrift* No. 58, (1893), "Contribution to the knowledge of the composition of wood from the pine trees, also the chemical process of manufacturing of cellulose" form the first real advance in Klason's wood chemical research, which comprises more than a hundred articles.

Klason attempted experimental research in conjunction with theoretical speculations in an effort to ascertain the nature of lignin and its chemical composition. He first thought that lignin was close to alizarin. Later on he supported its relationship with coniferin, and he considered it to be built up of coniferyl aldehyde.

During the first years of this century the interest in wood chemistry and wood pulp was very great and Klason found among his

assistants and pupils in his technical school of chemistry at KTH many competent fellow workers. It was also at this time that Klason received an appropriation for pure scientific research in this field. He published many of his papers in different periodicals in collected form under the title "Chemical-technical research about Sweden's most important wood." It comprised five volumes, the last one published as late as 1930. This collection contained other subjects from his pen as, for example, articles on arsenic, manufacturing of copper, etc.

Klason did not arrive at a definitive lignin formula, but he made a decisive contribution to the research in this field. Some workers have voiced various objections against his theories, but it is beyond doubt that without his research the chemistry of lignin of today would lack the foundations on which it was created.

Long after his retirement from his professorship at the Technical University Klason continued his research on lignin, partly as a teacher at Skogshogskolan for almost ten years, and partly at the laboratory through the generosity of his successor, Professor Carl Kullgrens. Up to the time of his death he had access to the chemical building of the new Technical University.

I have mentioned Klason's interest in Sweden's brewing industry which began when he served as controller at Klippans brewery; this interest served to identify Klason with zymurgy, a subject which he introduced at the technical university. His fearless action against the extreme temperance movement during the 1890's and, at the same time his support of a sound education which was essential in our land as a safeguard against the misuse of alcohol, pleased the brewing industry very much. Through this action he came in closer contact with the Swedish Brewery Association. He was their chairman for more than thirty years. The association presented to him a gold medal and elected him honorary chairman.

The Swedish Paper and Cellulose Engineers Society demonstrated the same honor in electing him honorary chairman and also bestowed upon him its first Ekman medal in gold.

Klason was also a member of many Swedish and foreign scientific associations. The Academy of Engineers nominated him as their first honorary member in 1920, and in 1943 a medal was stamped in commemoration of him.

In many ways his students at the Technical University demonstrated their high esteem for Klason. He was an excellent teacher and a rare educator who understood the problems of youth. He was not only a teacher of organic chemistry and chemical technology, but in his lectures and in the intimate talks with the students in the laboratory he expressed much of his philosophy of life, his interest in history, art, and political economy.

During a certain period of his life Klason was in rather delicate health. Among other things he was afflicted with phobias and was unable to fulfill his duties as lecturer which therefore were taken over by his assistants. In addition he was somewhat fretful, particularly during the examinations. There is no doubt that his wife's bright and happy outlook on life and endless patience to a great extent overcame the causes of his neuroses which ceased when he was sixty years old.

His two most characteristic attributes were an unyielding integrity and a diligence which was quite inconceivable. He imposed great demands upon himself and others. He gave very little of his time to social life and pleasure, but he put great store on spending his leisure time with persons of similar intellectual interests. He found these companions largely in the academy to which he belonged until 1889 when he was an assistant at the University of Lund.

Further evidence of his quest for intellectual stimulation was his membership in the society called "The Seventeen." There he met such prominent personalities as Oskar Montelius, C. Wahlgren, Yngve Sahlin, and many others. They met monthly in the homes of members in a friendly, informal atmosphere.

Klason was not a friend of modern literature. He read the great classics and such authors as Tegnér and Runeberg in the evenings after he had gone to bed. He quoted with pleasure in his lectures and speeches stanzas from the classics and one might conclude that his whole world of thought dealt with the philosophers of antiquity. But this was not so, as is evidenced by his lifework of practical realities.

A rather moving expression of his admiration for the great Greek thinker Socrates were his words to his son just before his death—indeed his last intelligible words. In the fall of 1936

Doctor Torsten Klason and his wife had made an automobile trip and among other places they had visited Athens. Knowing well his father's great interest in the culture of Greece, Torsten Klason tried in his letters to give a detailed description of everything he had seen and experienced. On his deathbed his father asked Torsten: "Did you see the place where Socrates stood before his judges?"

Thus might his last words form a conclusion to the description of Peter Klason's mission in life. With the assurance that he had made use of his talents he could with confidence and trust stand before the Almighty on Judgment Day. His industrious and productive life ended on January 1, 1937.

NOTES AND REFERENCES

Three appendices to the above article give details of Klason's work:

- 1 Erik Söderbäck, "Peter Klason's research on organic sulfur compounds," pp. 582-604.
- 2 Bror Holmberg, "Peter Klason's work on lignin chemistry," pp. 605-616.
- 3 Bibliography by Carl Björkbom, pp. 617-634.

(The last two items are the two articles of 1936 mentioned in the biography.)

From: *Levnadsteckningar över K. Svenska Vetenskapsakademiens ledamöter*, 142, 567-581, Stockholm, Almqvist & Wiksells, 1954.

Translated by Julia Christine Molander.

SIGURD NAUCKHOFF

.. 62 ..

Henry Edward Armstrong

1848-1937



HOW ARMSTRONG would have hated an orthodox memorial lecture about himself. And his memory is so fresh in the minds of his friends that it is difficult not to think of him as present with us tonight. How much we miss his active, fertile brain. In his Frankland Memorial Oration, the lessons of Frankland's career set him thinking, and in the last half of the lecture all Armstrong's pet hobbies appear—the failure of science in education, coal conservation, the problem of nutrition, the value of pure milk, the need for a survey of the world's natural resources—particularly phosphates—ending with a doubt as to the quality of the essay that members of the House of Commons would write on “No Life without Phosphorus.” Unfortunately he singled out Mr. Churchill, whose essay we have good reason to know would not be lacking either in appreciation of science or clarity of expression.

There is no need to chronicle the events of Armstrong's life, as that has been done already in the understanding study of his life by his collaborator and friend, his eldest son.

I cannot speak with the advantage of having been one of his pupils, although I was in a sense a step-pupil. I was fortunate to learn chemistry at Dulwich from H. B. Baker, to whom I can never be sufficiently grateful for having taught me both by precept and example that life without research loses much of its zest and excitement. Baker was one of the few schoolmasters who, like Frankland, managed to do research with very slender opportunities. We soon realized that Armstrong was one of his heroes, whose encouragement meant much to him. Baker often went to Lewisham on Sundays to talk over his problems with Armstrong, and on Monday mornings we heard all about it. This made us feel that we were in touch with what was going on in the great scientific world outside.

When the time came for me to be fattened, as Armstrong put it, for the University Shows, Baker told me to buy Armstrong's article on Inorganic Chemistry in the ninth edition of the *Encyclopædia Britannica*—and here it is. I have always kept it as a talisman,

as Kolbe kept his first letter from Berzelius. Written in 1876, when Mendeléeff's generalization was coming into prominence, it was almost the first consistent attempt to arrange the subject matter of chemistry in natural periods. I found it a most welcome relief from the formal textbooks, with its crisp, suggestive summary of each family of the elements, each illustrated with their more important heats of reaction.

I owe my first meeting with Armstrong, as I owe much else at Oxford, to Henry Miers' hospitality. It was rather a nervous moment for an undergraduate to meet Armstrong in his more leonine days. We knew he could be disconcerting. There was the story of the meeting at which there was a slight difference of opinion between the chairman and Armstrong as to the length and relevance of his remarks. When the next speaker began "Mr. Chairman and Gentlemen," Armstrong was heard to murmur. "A very proper distinction on this occasion." But Armstrong forgot that I was one of the "spoon-fed, over-taught, over-provided, over-examined, over-read and under-practiced products" when he heard I was a pupil of Miers and Baker, had been in Munich with Groth and had made geological excursions with Zittel and Rothpletz. I had many a stimulating talk with him, and a happy friendship of more than forty years was unmarred by any clash, although sometimes Armstrong must have been suspicious of my fancy for ions. Once when I spoke to the Science Masters' Association on the Theory of Ionic Dissociation, with Armstrong, an ex-President, sitting in the front row, everyone was expecting a thunderstorm at my expense; I think I escaped because Armstrong knew I was not dabbling in "fair hydrone" but in alcohol even drier than those vintages of which he was such a good judge.

We had many interests in common—crystallography, geology, scenery and John Ruskin. I think Armstrong forgave Ruskin for his hostility to modern science because of his love of crystals, his long study of the geological structure of scenery and his beautiful drawings. I remember what pleasure Armstrong got from Pope's gift of Cook and Wedderburn's Library Edition of Ruskin, with its reproductions of so many of Ruskin's own drawings. He was a great admirer of Ruskin's style and of his fearless advocacy of the

causes for which he cared. He thoroughly enjoyed the exuberance of Ruskin's purple passages, the eloquence of his defense of his heroes like Turner, and the invective with which he flayed the pretentious, the complacent, or the insincere. Armstrong, like Ruskin, would take infinite pains to find the right, the inevitable, word, and Ruskin had a genius for coining a word to emphasize his point. Of Sir John Lubbock's list of Best Hundred Books he wrote: "Putting my pen lightly through the needless . . . and blottesquely," as he did, "through the rubbish and poison of Sir John's list—I leave enough for a life's liberal reading." Armstrong probably felt a little envious, for he too was a great fighter.

The longest and most intimate talk I had with him was on a voyage to Morocco in 1936. It began by my asking him about the great chemists he had known in his younger days, and ended in a discussion of the history of organic chemistry when it was taking its modern form, which lasted until we reached Tangier. For me the talk was most revealing, as most of my impressions had come from Odling, Gerhardt's "Tami Odling," an enthusiast for the French school. Gerhardt and Laurent had always been my heroes. Armstrong, a pupil of Frankland and Kolbe, belonged to the other camp. Kolbe had always been a puzzle to me. I didn't know the story of his partnership with Frankland, and that talk with Armstrong revived an old interest and gave me a much clearer picture of the contributions of the two schools. When I was asked to give this lecture it seemed to me that it would not be inappropriate that the first of this series of lectures paying tribute to his memory should give a sketch of chemistry as Armstrong saw it in his student days and of the men under whose influence he grew up. I only hope I can recapture some of the life and color of the picture that Armstrong gave me.

For Armstrong the history of chemistry was not just a succession of theories, as it is so often painted. He was interested in the personalities of the chemists who made them, their characters, and their practical contributions to the corpus of chemical knowledge. In the period we discussed, the efforts of almost all the outstanding chemists were directed to organic chemistry. It was a period of rapid growth, when there were great discoveries to be made by

individuals. Each had his own theory of which he was tenacious, as it meant much to him; it was in a sense the scaffolding which enabled him to make his individual contribution to the structure of chemistry. And Armstrong judged not by the theory but by the results. "By their fruits ye shall know them." And was it not Armstrong who said that "Hypotheses like Professors, when they are seen not to work any longer in the laboratory, should disappear"?

The best landmarks of progress in these years are the great textbooks, not those written by compilers such as Gmelin, useful as they were, but those written by the men who were reshaping organic chemistry in the laboratory, and felt the urge and had the energy and imagination to give their picture of the whole range of the subject. Those milestones were the third edition of the great *Lehrbuch* of Berzelius translated by Wöhler in the years 1833 to 1841, in which organic substances are classified under their various plant or vegetable origins; Liebig's textbook of 1839 which opens with a brave phrase, echoing Lavoisier, "Organic chemistry is the chemistry of compound radicals," but after starting with compound radicals as a basis of classification he soon relapses into the Berzelian system; Gerhardt's *Précis* of 1844, using his own classification based on homologous series, his "Introduction to Chemistry by the Unitary Method" of 1848, and the four volumes of his *Traité* of 1853-56; Kolbe's textbook of 1854-60, written with his shrewd insight into the structure of organic acids; and finally Kekulé's unfinished *Lehrbuch* of 1859-67 in which organic chemistry began to take its modern form. Here they are as a visual record of Armstrong's conversation during those three unforgettable days.

He began with Laurent and Gerhardt, the two young rebels who saw the weakness of the Berzelian system, and gave their lives to remodelling organic chemistry and giving it a scientific classification based once again on the clear logic of a French mind. Here I was able to contribute something from my many talks with Odling. Armstrong admired the courage and tenacity with which Gerhardt and Laurent fought tradition and authority, fearless of the effects on their personal fortunes, but he deplored the completeness of

their ultimate victory which he felt had obscured progress by preventing a full appreciation of the work of Frankland and Kolbe. For me their's is one of the epic partnerships, to be ranked with Lavoisier and Laplace, Liebig and Wöhler, and I would now add Kolbe and Frankland. They suffered almost persecution for their views, and Laurent died as a result of great privation. Their laboratory researches were carried out under incredible difficulties and lack of support, but they had the unquenchable fire of devotion to chemistry.

Laurent, the elder by eight years, was the son of a peasant, Trained as a mining engineer, in 1831, at the age of twenty-four, he was Dumas' lecture assistant, and was working with him on naphthalene and its derivatives. Armstrong was interested in him as one of the earliest chemical crystallographers, for besides preparing a large number of new substitution derivatives of naphthalene he measured their crystalline form and showed that they formed an isomorphous series. This gave added support to the view of the French chemists that in these substitution products chlorine occupied the same position as the hydrogen it replaced. It was probably also the basis of Laurent's theory of nuclei in which he pictured a parent structure with carbon atoms at the angles of a regular polyhedron and hydrogen atoms at the middle of each side replaceable by other groups, with the possibility of additive compounds corresponding to pyramids on the faces. Laurent's nuclei were comparable with Dumas' types, with the added hypothesis of the geometrical structure of the molecules.

Laurent is remembered for his association with Gerhardt and the important influence he had on Gerhardt's views, but he was a most skillful organic chemist, and he added greatly to our knowledge of many groups of organic compounds.

Gerhardt, born in 1816, was the son of an Alsatian chemical manufacturer. He published his first paper, on the classification of silicates, when he was eighteen, and finding the routine of his father's business intolerable, with the help of friends he spent two years with Liebig at Giessen. Returning home he quarrelled once again with his father and set out, at the age of twenty-three, to seek his chemical fortune in Paris, armed with a letter to Dumas

from Liebig and 200 francs in his pocket. He kept himself by doing literary work, including the translation of Liebig's textbook, which gave him a wide view of the whole range of organic chemistry as it then was.

Right from the outset Gerhardt seemed to realize the need for some entirely new approach to the problems that were presented by the rapidly growing number of organic compounds. In most of his papers there is an attempt at a generalization, often based, so his opponents said, on insufficient evidence, but Gerhardt had the same sort of vision of a new system as Lavoisier, and each of his main papers marked a step toward the reorganization of organic chemistry at which he aimed.

By 1840 the battle over substitution had been won and the authority of Berzelius had begun to be seriously challenged. For Berzelius as for Lavoisier oxygen was the central element. His massive contribution to chemistry had been built up on Lavoisier's dualistic conception of chemistry, reinforced by the electrochemical theory of chemical affinity. The elements of organic chemistry, for Berzelius as for Lavoisier, were the compound radicals, into whose composition oxygen could not enter, as by definition a radical is an oxide less oxygen. Thus Berzelius wrote the formula of acetic acid $C_4H_6O_3 \cdot H_2O$, a combination of the oxide of the radical C_4H_6 with water, which in the acetates was replaced by metallic oxides. That electronegative and electropositive elements like chlorine and hydrogen could occupy the same place in chemical compounds was unthinkable for Berzelius.

But now dualism, the electrochemical theory and Berzelius' conception of radicals had received a severe blow. Even Berzelius' atomic weights were being replaced by those of Gmelin in which the values for carbon and oxygen were halved to make them 6 and 8, respectively. Dumas, Laurent, and others had shown that electronegative elements like chlorine could replace hydrogen atom for atom in organic compounds with little change in properties and, as Laurent showed, without change of crystalline form. Berzelius fought hard against the idea that such a replacement could take place, and assumed that the substitution was accompanied by a change of structure. He gave acetic acid the formula $C_4H_6O_3 \cdot H_2O$

and trichloroacetic acid $\text{C}_2\text{Cl}_6.\text{C}_2\text{O}_3.\text{H}_2\text{O}$. But the facts were against him, and in 1840 he seized on Gerhardt's conception of bodies like nitrobenzene as conjugate compounds formed by the union of two residues with the elimination of water, the organic radical being called by Gerhardt a "copula." Berzelius' formulas now became conjugate, and substitution was admitted in the copula. Acetic acid was written as $\text{C}_2\text{H}_6.\text{C}_2\text{O}_3.\text{H}_2\text{O}$ and trichloroacetic acid $\text{C}_2\text{Cl}_6.\text{C}_2\text{O}_3.\text{H}_2\text{O}$. And so conjugate compounds and copulas, Berzelius' practical admission of defeat, took their place in chemical literature for twenty years. In the hands of Kolbe they were made the basis of an important contribution to structural chemistry.

Gerhardt's paper on nitro compounds which started the idea of conjugate compounds and copulas was followed by work on cyclo-mene derivatives which gave him the notion of homologous series of organic compounds. This was the basis of a revolutionary paper in 1842 on the classification of organic substances. Gerhardt now saw the need to ensure that formulas should represent comparable magnitudes. These had been based previously to a large extent on the theory of dualism which he rejected. Following Ampère he insisted that the weights of equal volumes of vapor must represent comparable magnitudes and he first adopted four-volume formulas referred to one volume of hydrogen as unit. But later, realizing that inorganic formulas were on a two-volume basis, he made this the basis of his organic formulas, and he doubled the Gmelin equivalents for carbon and oxygen, thus arriving at practically the same values of molecular and atomic weights as we use today.

In 1844 he published the first volume of his "Précis de Chimie Organique" using the homologous series as the basis of classification together with the chemical families of compounds which contain the same number of carbon atoms and can be derived from one another. Gerhardt having lost faith in dualism, the electrochemical theory, and the Berzelian radicals, turned to a purely empirical outlook, thus avoiding the hypothetical formulas of other chemists, which he regarded as figments of the imagination. He used empirical formulas based on a two-volume basis and he used the word "equivalent" indiscriminately for atomic, molecular, and equivalent weights.

The new views roused a storm of opposition from the older chemists, and Berzelius did his best to discredit them in the *Jahresbericht* in which he had reviewed the current chemical literature since 1822. Gerhardt, undaunted by this formidable opposition, determined to get a hearing for his own point of view. In 1845 he founded a new journal, "*Comptes Rendus mensuels de Travaux Chimiques*," which contained both original papers and a summary by himself of current literature which gave him the opportunity of replying to Berzelius. It was a courageous venture in view of Gerhardt's slender resources, but with his indomitable energy he produced the new journal, completed the second volume of the *Précis*, and carried on his laboratory researches single-handed.

In 1844 Gerhardt and Laurent had decided to collaborate. It was a fortunate and stimulating partnership, for Laurent like Gerhardt was seeking a logical basis of classification along rather different lines, and Gerhardt's impetuosity gained much from Laurent's better balanced judgment. Gerhardt had gone too far in his reaction against the older theories, in his use of purely empirical formulas and his neglect of any distinction between atoms and molecules. Laurent pointed this out to him, and Laurent's own constructive contribution to the new system came in 1846 in a paper on the organic compounds of nitrogen. In this he supports Gerhardt's two-volume formulas, and points out that in these formulas the sum of the atoms of hydrogen, nitrogen, and the halogens is always an even number. The examination of apparent exceptions to this rule showed that they were based on incorrect analyses, and numerous revisions of formulas were suggested.

Laurent then applied the two-volume formulas to elementary gases, and showed that their molecules must contain two atoms, which led him to the modern definitions of atom, molecule, and equivalent, and to the explanation of nascent action, which until then had been a mystery.

In 1848 came Gerhardt's final blow at dualism in his "*Introduction à l'étude de la Chimie par le système unitaire*," in which he classes substances both according to their chemical functions and in homologous series. He uses unitary formulas, and is still skepti-

cal about Laurent's definition of atoms and molecules. He uses the term "proportional number" for both.

Gerhardt's violent reaction against the welter of formulas was natural. For most of them had no practical justification, and in his eyes they merely darkened knowledge. But Laurent now convinced him that he had gone too far in using only empirical formulas, as there certainly were groups of atoms which were transferred from one compound to another in chemical reactions and Gerhardt had already admitted this in his conception of residues and copulæ. It was along these lines that their so-called synoptic formulas were developed.

Their collaboration at this time was difficult, as Gerhardt was in Montpellier and Laurent in Bordeaux, and they met only once. They were eager to be working together in Paris, but the opposition to their views was intense and they were regarded almost as dangerous criminals by the older chemists who controlled all chemical appointments. When Laurent applied for posts, on two occasions they were given to Balard—"Balard who was discovered by bromine" was Laurent's bitter comment.

They criticized Liebig's work on the derivatives of melanine, and particularly his analysis and formula of mellone. Liebig was furious and published a tract "*M. Gerhardt et la Chimie Organique*," in which he called Gerhardt a highway robber and accused him of stealing other people's belongings and using them himself. Liebig also tried to break up the partnership by telling Laurent that Gerhardt was "*un homme sans moralité*" and others warned Laurent that his association with Gerhardt would ruin his prospects.

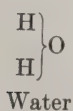
But Laurent's loyalty to Gerhardt was superb. He was now in Paris without an appointment, living by giving lectures and often in great want, but he never hesitated to take Gerhardt's quarrel on his own shoulders. There is a pathetic letter to Gerhardt saying that he has no alcohol or ether and must stop work unless Gerhardt can authorize him to buy 20 francs' worth of chemicals on his account. In another he says, "Poverty has just made me commit a crime—I have sold Masson a bad book on crystallography and the blowpipe for 500 francs."

In 1848 Gerhardt got a year's leave from Montpellier without

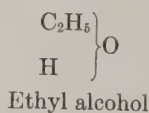
salary in order to be with Laurent in Paris. In the following year, as no appointment was forthcoming and Laurent had lost a small post he had at the Mint, owing to ill-health, Gerhardt borrowed some money and with Laurent opened a small laboratory where they could work together and make a living by taking pupils. Meanwhile their views were steadily gaining adherents, particularly in England, where Williamson was a stout friend and supporter.

Then came a series of discoveries in other laboratories which had a decisive effect on the development of Gerhardt's views. In 1849 Wurtz prepared the primary amines by the hydrolysis of isocyanates. In the following year Hofmann isolated the primary, secondary, and tertiary amines by the action of ammonia on alkyl iodides, and in the same year came Williamson's historic paper on etherification and his synthesis of ethers by the action of alkyl iodides on the alcoholates of potassium.

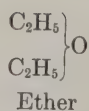
The formulas of alcohol and ether and their chemical relationship had been in hot debate for a quarter of a century, and Williamson now established the correctness of Gerhardt's view of their relative molecular magnitudes. He wrote their formulas as derivatives of water by the successive replacement of hydrogen by ethyl thus:



Water



Ethyl alcohol



Ether

Odling often told me that his contemporaries were never convinced about physical methods for determining molecular weights, but they accepted Williamson's chemical proof of the relative magnitudes of alcohol and ether as decisive. His notes for a lecture I persuaded him to give at Oxford in 1899 on "Chemical Theories under Discussion about the year 1850" contain the following passage: "Dependency then of determination of atomic weights on possibility of determining unit weights—means for determination of unit weights. Conclusions from gas or vapour densities and other physical considerations. Deduction of molecular or unit weight scarcely accepted by physicists and not at all by chemists. Necessity for determination of unit-weights on chemical grounds for

establishment of concordance of results with those based on physical grounds."

Gerhardt was no mere theorist as his enemies liked to make out. During these years in Paris, in spite of their difficulties, he and Laurent had a big output of research and the decisive moment came for Gerhardt with his synthesis of the anhydrides of monobasic acids in 1852. Hitherto, apart from Deville's preparation of nitric anhydride, the only anhydrides which had been isolated were those of dibasic acids such as sulfuric and succinic in agreement with Gerhardt's formulas, although dualistic formulas made the existence of monobasic anhydrides equally probable. Gerhardt by the reaction of acid chlorides with the alkali salts of monobasic acids succeeded in preparing a whole series of anhydrides. It was a parallel to Williamson's work on the ethers, when the method of preparation was conclusive evidence of their formulas.

Not only was Gerhardt's work a final proof of the untenability of the dualistic formulas for monobasic acids, but the similarity with the ethers set him thinking, and the paper contains the first statement of his theory of types in which he referred the formulas of organic compounds to four types: water, hydrogen, hydrochloric acid, and ammonia. By the substitution of various organic groupings for hydrogen the different classes of organic compounds could all be represented as derived from these simple inorganic molecules, thus giving a new method of classifying them and showing the relationships of their chemical composition. Gerhardt's type formulas were an unconscious recognition of the different combining powers of the atoms and groups, and led inevitably, I had always thought, to Kekulé's theory of atom linkage.

At this point, when we were discussing the influence of Williamson on Gerhardt, I fortunately asked Armstrong a question that he evidently regarded as very ill-informed. Forgetting for a moment the baptismal names of his first-born and his own early master, I asked whether he thought that Williamson or Frankland had made the greater contribution to chemistry. I was quickly left in no doubt as to his opinion, and only hunger ended his recital of the Kolbe-Frankland saga. No doubt the story was told in full in his Frankland Memorial Lecture, but the manuscript of this was

unfortunately lost so I must try and reconstruct it from what Armstrong told me.

Till then Kolbe had always been an enigma to me, as I daresay he is to others. It seems so difficult to reconcile his queer formulas, his apparent conservatism, and his violent attacks on Kekulé and van't Hoff, with his success as a teacher and his great contribution to structural chemistry. Born in 1818, the son of a clergyman, Kolbe's training was under Wöhler at Göttingen, where he met Berzelius and was no doubt brought up by Wöhler in the true Berzelius tradition. His early work with Wöhler was on the chlorination of carbon disulfide to give thiophosgene and carbon tetrachloride. From the former he prepared a series of chlorinated methylsulfonic acids which, following Berzelius, he formulated as conjugate compounds with the radical methyl acting as a copula. Berzelius was delighted at the discovery of a series of analogs to the chloracetic acids. He devoted six pages of the *Jahresbericht* to Kolbe's paper, and won his heart by writing him an encouraging letter which Kolbe kept as a talisman all his life. There is little doubt that the success of this investigation colored the whole of Kolbe's life's work and outlook.

For Gerhardt, rational formulas were only a convenient means of representing the reactions in which a substance might take part, and the same substance could have more than one rational formula. Even Kekulé as late as 1861 still kept this Gerhardtian view. But for Kolbe the conjugate formulas of Berzelius, adapted as we have seen from Gerhardt, meant something real and he set out to try and prove their truth both by analysis and synthesis. Encouraged by the early success of his experiments he never wavered from this view, and this explains both his conservatism and the motive power behind his researches. Kolbe had also obtained trichloracetic acid by passing carbon tetrachloride through a heated tube, and hydrolyzing the resulting tetrachlorethylene in presence of chlorine. This was one of the earliest examples of the synthesis of an organic compound from its elements. Most of this work was done in Marburg, where Kolbe had gone in 1842 as Bunsen's assistant, and had learned his methods of gas analysis. In 1845 he came to London as assistant to Lyon Playfair, to carry out the

analysis of mine gases for the Commission that was sitting on explosions in coal mines. There he met Frankland, who had just been appointed by Playfair as junior assistant to undertake the analysis of minerals at the School of Geology in Jermyn Street.

Frankland, who was then twenty years old, had begun his chemical career, like Dumas, as a druggist's apprentice. This had taught him little, but a Lancaster surgeon named Johnson, realizing the lack of training of apprentices like Frankland, had made a small laboratory and lecture room to encourage them, and took an active interest in their studies. Struck by Frankland's keenness and ability he got an introduction for him to Lyon Playfair, and then, as Armstrong said, Frankland began "to learn chemistry on the Squeer's principle by making it." Within two years, with the help of Kolbe, he was making chemical history.

Kolbe's heart was in organic chemistry, not gas analysis, He wanted to discover the groupings in an organic compound, to prove the existence of the radicals which Berzelius called copulas. His first success came when he isolated the butyl radical (actually octane) by the electrolysis of a strong solution of valeric acid. He quickly interested the young Frankland in organic chemistry, and together they began a research to try and establish the molecular structure of the fatty acids by synthesis. They prepared ethyl cyanide and on hydrolysis it gave, as they hoped, propionic acid (they called it metacetic acid), thus proving the existence of the ethyl radical in the acid. Once again the success of a first research was the turning point in a career. When Kolbe returned to Marburg he took Frankland with him to continue their joint research and to learn gas analysis from Bunsen. They first extended their work to methyl and amyl cyanides which gave, as they expected, acetic and caproic acids on hydrolysis. They then tried to isolate the radical ethyl by the action of potassium on ethyl cyanide; they failed to do this but discovered an interesting polymer of ethyl cyanide and investigated its derivatives. After three months in Marburg, Frankland had to return to England to teach chemistry at Queenwood College, a school in Hampshire, where Tyndall was his colleague. There he continued his attempts to isolate hydrocarbon radicals by heating ethyl iodide in sealed tubes with po-

tassium, when he got a mixture of ethylene and ethyl hydride. The experiment was repeated using zinc in place of potassium, but a violent explosion during the analysis of the resulting gas shattered Frankland's eudiometer, and his experiments were held up until he went again to Marburg with Tyndall in the autumn of 1848. Analysis then showed that he had isolated what he called ethyl, which was in fact butane. He continued the work with ethyl and methyl iodides, studying the reactions of the halogens with the hydrocarbon radicals until, on July 12, 1849, in Marburg, came the dramatic discovery of zinc methyl, the first of the organo-metallic compounds. Frankland had added water to the solid residue left after heating methyl iodide with zinc, when a greenish-blue flame several feet long shot out of the tube causing great excitement in the laboratory. Bunsen was at first alarmed lest it should be cacodyl, due to an impurity of arsenic in the zinc, but it was quickly found that the metallic constituent was zinc, and the formula of the new substance proved to be $\text{Zn}(\text{CH}_3)_2$.

Shortly afterward Frankland was invited by Liebig to spend a semester at Giessen, and there he isolated the radical amyl and began to work on zinc amyl. At the end of the year he returned to England to take Playfair's place as professor at the Civil Engineering College at Putney until 1851, when he went as the first professor of chemistry to the newly founded Owens College in Manchester, where he remained until 1857.

Frankland was quick to see that his discovery of zinc methyl opened up a wide field of research, and he first prepared a number of the alkyl compounds with zinc and tin and later with mercury and boron and made a most careful and systematic study of their properties. He soon realized their importance as synthetic reagents—zinc methyl, he said, "will be capable of replacing electronegative elements in organic or inorganic compounds by ethyl—a kind of replacement which has never yet been attempted, but which the author anticipates will enable him to build up organic compounds from inorganic ones and ascend the homologous series of organic bodies." Frankland was the pioneer in using the organo-metallic compounds in organic synthesis for the next twenty years.

Armstrong often spoke of Frankland's extraordinary practical

ability. "I have never met with a more skillful worker, and those early papers of Frankland's in a new and most difficult field bear witness to his great experimental skill and originality. He was a great thinker too, and within three years of his discovery of zinc methyl his study of its analog led him to the first general statement about the combining powers of the elements, afterward known as the theory of valency."

Zinc methyl was similar in constitution to Bunsen's cacodyl which Kolbe regarded as a conjugate compound of arsenic with methyl as a copula. Now according to Berzelius the presence of a copula should not alter the combining power of an element or group: acetic acid for instance had the same basicity as formic acid in spite of the presence of the methyl copula. Cacodyl like arsenic combined with oxygen and the halogens and formed an acid. Hence Frankland expected zinc methyl to behave similarly and was surprised to find that it had no combining power, merely exchanging its hydrocarbon groups for others. A study of the properties of stannous and stannic ethides, and a comparison of the formulas of cacodyl and organic antimony compounds convinced him that elements had a definite combining power and that the attachment of each methyl group reduced by one their power to combine with other elements. "No matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed to use the term, is always satisfied by the same number of these atoms."

The paper containing this generalization which was to transform chemical theory was communicated to the Royal Society in May, 1852, but was not published for twelve months as it was mislaid by the Secretary (Professor, afterwards Sir, Gabriel Stokes), and Frankland thought it had not been thought worthy of publication. A delay at this critical moment was most unfortunate as, to quote Armstrong, "the problem first solved by Frankland was in the air—chemists everywhere had it in mind, especially in France." Gerhardt's types were a partial recognition of the same principle, extended by Williamson to multiple types with polyvalent radicals, the valency or atomicity of which was first indicated by Odling by the familiar dashes. But Frankland was the

first to see that there is a general law of atomicity or valency underlying chemical combination.

Meanwhile Kolbe had left Marburg in 1851 to spend three years in editing Liebig's and Wöhler's "Dictionary of Chemistry" for Vieweg, and in 1854 the first part of his "Textbook of Organic Chemistry" was published. In the introduction he makes his own position quite clear. He still regards the radical theory as the safest basis for teaching chemistry and says that he belongs to the conservative party of chemists. He attacks Gerhardt and Laurent for their unsound generalizations, and for the type theory. "Chemistry is something more than a mere arithmetical exercise into which Laurent and Gerhardt think they can convert it." He attacks Williamson's and Gerhardt's formulas for alcohol and ether on the ground of the products of electrolysis of alcoholates. He refuses even to accept Frankland's ideas on atomicity, as he would not admit that electronegative elements could be replaced by electropositive radicals such as methyl and ethyl. His formulas are based on dualism using Berzelius' copulas and Gmelin's equivalents. Not, it would seem, a promising beginning! But Kolbe's strength was in the laboratory and he collects for the first time in one chapter all the methods of preparing derivatives of organic compounds by means of chemical reagents, which have since become standard:—oxygen and oxidizing agents, reducing agents, halogens, phosphorus pentachloride and oxychloride, nitric and nitrous acids, and sulfuric acid. His classification of compounds is partly by radicals and partly by acids and their derivatives, to our knowledge of which he was to contribute so much.

The difference of opinion between Kolbe and Frankland was soon settled by correspondence between them. Kolbe accepted Frankland's theory and in 1857 they published a paper "On the Constitution of the Fatty and Aromatic Acids, Aldehydes, Ketones, etc., and their Relation to Carbonic Anhydride," giving their joint view that the oxygen atoms in oxides of metals and nonmetals can be replaced by the same number of atoms of a positive atom or radical, the replacement being accompanied by an increase in the base properties of the compound. (Frankland's name was accidentally omitted as a joint author with Kolbe, but the paper

throughout uses the pronoun "we.") Thus Frankland had an important influence in changing Kolbe's outlook and even before their joint paper Kolbe was teaching that organic compounds can be regarded as derived from carbonic acid by the replacement of oxygen atoms by radicals. In this he was following a suggestion made by Liebig in 1847 in a paper on the chemical processes underlying respiration. Kolbe elaborated the theory in 1860 in his classical paper on "The Natural Relation between Organic and Inorganic Compounds," and it was the basis of his pioneer work which revealed the structure of so many organic compounds.

Using atomic weights of 6, 8, 16 and 35.5 for carbon, oxygen, sulfur, and chlorine, respectively, he first wrote formulas as follows:

Dibasic carbonic acid	$2\text{HO} \cdot \text{C}_2\text{O}_4$
Monobasic methyl carbonic or acetic acid	$\text{HO} \cdot \text{C}_2(\text{C}_2\text{H}_3)\text{O}_3$
Acetic aldehyde	$\text{C}_2(\text{C}_2\text{H}_3)\text{H} \cdot \text{O}_2$
Acetone	$\text{C}_2(\text{C}_2\text{H}_5) \cdot \text{O}_2$

Then realizing that the basicity of the acid was related to only two of oxygen atoms in C_2O_4 since it vanished when these two were replaced by other atoms or radicals, he distinguished between the oxygen inside and outside the radical $[\text{C}_2\text{O}_2]$ to which he gave the name carbonyl:

Carbonic acid	$2\text{HO} \cdot$	$[\text{C}_2\text{O}_2], \text{O}_2$
Formic acid	$\text{HO} \cdot \text{H}$	$[\text{C}_2\text{O}_2], \text{O}$
Acetic acid	$\text{HO} \cdot (\text{C}_2\text{H})$	$[\text{C}_2\text{O}_2], \text{O}$
Acetaldehyde	$\text{H}_2\text{C}_3 \}$	$[\text{C}_2\text{O}_2]$
	H	
Ethyl alcohol	$\text{HO} \cdot \left\{ \begin{array}{l} \text{C}_2\text{H}_3 \\ \text{H}_2 \end{array} \right\}$	C_2, O
Unknown alcohols	$\text{HO} \cdot \left\{ \begin{array}{l} \text{C}_2\text{H}_3 \\ \text{C}_2\text{H}_3 \\ \text{H} \end{array} \right\}$	$\text{C}_2, \text{O} \quad "$
Propionic acid	$\text{HO} \cdot \left\{ \begin{array}{l} \text{C}_2\text{H}_3 \\ \text{C}_2\text{H}_3 \\ \text{C}_2\text{H}_3 \end{array} \right\}$	C_2, O
Propionic acid	$\text{HO} \cdot (\text{C}_4\text{H})$	$[\text{C}_2\text{O}_2], \text{O}$
Lactic acid	$\text{HO} \cdot \left(\text{C}_4 \left\{ \begin{array}{l} \text{H}_4 \\ \text{HO}_2 \end{array} \right\} \right)$	$[\text{C}_2\text{O}_2], \text{O}$
Glyceric acid	$\text{HO} \cdot \left(\text{C}_4 \left\{ \begin{array}{l} \text{H}_3 \\ \text{HO}_2 \\ \text{HO}_2 \end{array} \right\} \right)$	$[\text{C}_2\text{O}_2], \text{O}$

These formulas, clumsy as they may seem to us, were based on Kolbe's own study of organic compounds and their synthesis. They had a very real significance for him and by comparison he considered Gerhardt's type formulas superficial and lacking in any fundamental basis. Having always two atoms of carbon in place of one must have made it difficult for him to appreciate the theory of atomic linkage, but he used his formulas with an uncanny instinct to predict the existence of unknown compounds, such as the secondary alcohols discovered by Friedel in 1862 and the tertiary alcohols by Butlerow in 1864, using Frankland's zinc methyl as a synthetic reagent. But more important still was the use he made of them in directing the research in his own laboratory to the elucidation of the structure of more complex organic substances. Outstanding examples of this are: the reduction of malic and tartaric acids to succinic by Schmitt in 1860, Kolbe's own researches on the constitution of lactic acid and alanin, and his synthesis of taurine in 1862, Volhard's synthesis of sarcosine in the same year, von Oefele's discovery of the sulfine and sulfone compounds in 1864, Kolbe's synthesis of malonic acid from cyanacetic acid in the same year, and finally his synthesis of salicylic acid and his discovery of nitromethane almost simultaneously with Victor Meyer.

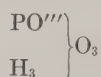
While Kolbe was making these outstanding contributions to the synthesis of organic acids and to our knowledge of their constitution, Frankland was also active in the same field. In 1857 he left Manchester to get more time for research at St. Bartholomew's Hospital and in 1863 he succeeded Faraday at the Royal Institution.

With the help of the zinc alkyls Frankland, working with Duppa, synthesized a number of new members of the lactic acid series from which they prepared the corresponding acrylic acids and their derivatives. Finding that when ethyl acetate is heated with sodium a large volume of hydrogen is evolved they determined to utilize this reaction for the synthesis of higher members of the fatty acid series. In the course of this work they isolated acetoacetic ester independently of Geuther and used it to synthesize a large number of fatty acids, ketones, and ketonic esters.

Thus both Kolbe and Frankland, working outward from their early joint researches on independent lines, made a great contribution to synthetic chemistry just at the time when the theory of atomic linkage enabled such knowledge to be applied to the structure of organic chemistry. When Duppa died in 1873 Frankland's interest in organic chemistry seemed to lapse, but Kolbe was active until his death in 1884.

When the Kolbe-Frankland saga was ended Armstrong and I went back to where we had left Gerhardt and Williamson and the type theory in 1853, when Kekulé, the maker of modern organic chemistry, was just coming on the scene.

Gerhardt's types had an immediate success with the younger chemists. Williamson at once extended them to include multiple types to cover the case of polyatomic radicals and polybasic acids:



Odling introduced mixed types and indicated the atomicity of the radicals by the well-known dashes.

It was tragic that Laurent should have died in 1853 just when the long fight was practically over and Gerhardt's system to which he had contributed so much was winning general acceptance. Laurent had sacrificed everything for science and had achieved so much in the face of great difficulties. He died exhausted by the long struggle against poverty and against almost fanatical opposition.

In 1854 Gerhardt tasted success. He was appointed to a professorship at Strasbourg, where he was to build a new laboratory, and by the irony of fate he was asked to write the new edition of Berzelius' "Organic Chemistry." He accepted on condition that he could use his own classification in homologous series and chemical families, but at long last he had learnt the value of compromise. Only in the final chapters on Generalities does he use his type formulas and his own atomic weights; in the body of the work he uses Gmelin numbers and even gives the dualistic formulas. When Pebal asked him why he had not used his own clearer presentation

throughout, he laughed and answered, "Then nobody would have bought my book!"

In the final chapters he expounds his type theory, and shows how the formulas of organic substances can be derived from four types by the substitution of hydrogen by radicals or residues. Radicals he defined as groups of atoms which can be exchanged in double decompositions but cannot be isolated. "Chemical formulæ are not intended to represent the arrangement of the atoms in a molecule, but their object is to show in the simplest and most exact way the relation between substances." Gerhardt regarded his formulas as contracted chemical equations, and while therefore substances might have more than one formula, most could in fact be represented by only one.

These chapters were his last legacy to science, as he died suddenly in 1856, when he was correcting the proofs, at the age of forty.

Gerhardt's interest was in classification, in finding a system within which the rapidly growing multiplicity of organic compounds would find their logical place, thus making possible the scientific study of their properties and relationships. He was skeptical as to the possibility of ever knowing the actual atomic structures of molecules. His formulas were formulas of convenience, but the progress he had made and the order he and Laurent had introduced were destined very quickly in the hands of Kekulé to give organic chemistry its modern form.

Kekulé after studying chemistry under Liebig from 1849 to 1851 spent a year in Paris, where he met Gerhardt who gave him the manuscript of his treatise to read. This left a lasting impression on him, and as Armstrong said "he was enthralled by Gerhardt." In 1853 he came to London as assistant to Stenhouse who was then Chemist to the Mint. In London he saw a great deal of Williamson and Odling, both enthusiasts of the Gerhardt school, and he always said that his structural theory was born in his dream about atoms on the top of an omnibus between Islington and Clapham Road, where he lodged. In 1856 he went to Heidelberg as *Privatdozent*, and his investigations of the constitution of mercury fulminate led him in 1857 to recognize the tetravalency

of carbon and to add to Gerhardt's types the marsh gas type. In 1858 he developed the idea at length in a paper on "The Constitution and Metamorphosis of Chemical Compounds and the Chemical Nature of Carbon," and the first parts of his *Lehrbuch* were published in 1859.

Kekulé recognizes at the outset that the hydrogen, water, and ammonia types, to which he had added the marsh gas type, are only the recognition or expression of the combining powers of the elements or radicals, and he uses Odling's dashes to indicate their atomicity or basicity or what we call valency—but he made no reference to Frankland. His rational formulas are based on Gerhardt's types, and he explains in almost the same words as Gerhardt that these rational formulas are only reaction formulas, not constitutional formulas, and that they do not express the relative positions of the atoms in the compound. He emphasizes this "as some chemists seem to think that they can determine the constitution of compounds from their reactions." In any case, says Kekulé, this would need a perspective drawing and cannot be shown by the arrangement of atoms in one plane. Chemistry, he said, will never reveal the structure of the molecule, but possibly physics may.

When Kekulé comes to consider the carbon compounds in detail his great advance was the recognition of the formation of carbon chains with either single or multiple links between the carbon atoms, but he did not seem to realize the power of the instrument he had constructed. He wrote a few graphic formulas for two carbon bodies, such as acetic acid, which show accurately their constitution for the first time on a valency basis. He realizes that the properties of the atoms are dependent on their relative position in the molecule, and yet he does not apply these formulas to substances containing three carbon atoms when they would have explained the isomerism of the lactic acids, as he says that they cannot give a true picture of the positions of the atoms. The isomerism of ethylene dichloride and ethylidene dichloride is left unsolved when the solution is ready at hand if he had used his graphic formulas consistently. He criticizes the use of the formulas used by Kolbe in which the difference between alcoholic

and acidic hydrogen is explained. "Such formulæ have no advantage," he says, "over the type formulæ, they conceal a number of analogies and in other cases suggest analogies where none exist."

All this shows Kekulé was suffering from what Armstrong called "Gerhardtism," and that at this time he did not realize the full value of the new instrument he had put into chemists' hands. Gradually its value dawned on him, and he used it with greater confidence. The first volume of the *Lehrbuch* was completed in 1861, the second volume on aromatic compounds based on Kekulé's benzene ring appeared in 1866, and the third volume was never finished. Kekulé gave organic chemistry its modern form and fifty years later physical analysis, as he had predicted, established the reality of the formulas as to which he was at first so skeptical.

Kolbe never forgave Kekulé for his advocacy of Gerhardt's type theory, for his failure in the *Lehrbuch* to make any recognition of Frankland's contribution to the theory of valency or atomicity, and for his rather scornful reference to Kolbe's own work. For twenty years he lost no opportunity of attacking Kekulé's views and giving Frankland the credit that was his due. It is a curious example of how far personal ties can warp the judgment of one who had himself made such great contributions in the same field. Armstrong said that when he left Kolbe early in 1870 "he was already peculiar; he afterwards, in his last years, so fixed his mind upon certain grievances as to be little short of a monomaniac." Victor Meyer, and there can be no better judge, sums up the Kolbe paradox in a sentence: "Zwar wurde Kolbe in seinen späteren Jahren ein unermüdliche Bekämpfer der Valenztheorie, doch hat grade er in erster Linie zur Klarlegung des Valenzbegriffs beigetragen."

Armstrong's final word on the Kolbe-Kekulé controversy was in his review in *Nature* of Anschütz's "Life of Kekulé": "Nothing is more certain than that most of us only take in new ideas through experience—the want must be felt before it can be satisfied. Once assimilated, an idea is expelled or modified with great difficulty. It is that that makes scientific thought, the scientific habit of mind, so difficult of attainment. Kekulé at once fell victim to Gerhardt's magic influence, when he met him in Paris. His belief in Ger-

hardt's system became strengthened, in London, through association with Williamson and Odling. He does not seem to have been intimate with Frankland. He appears to have been so satisfied with the superiority of Gerhardt's system, that he took little, if any, notice of Kolbe's work: I do not believe that he ever mastered the inner meaning of Kolbe's formulæ. Kolbe had little use for the Gerhardt formulæ, knowing that he had penetrated deeper than they carried him. I feel sure he resented the way in which he and Frankland were waved aside by Kekulé: and probably, this was the subconscious, if not conscious, primary cause of the bitterness he displayed towards him, in later life. In addition he was a linguistic purist and idealist, and was greatly annoyed by Kekulé's at times flamboyant masterful style. As I have said elsewhere, Kolbe's doctrine was ever the Pauline 'Alles prüfen'—Prove all things! He took exception, therefore, to what he thought to be Kekulé's dogmatic, if not arrogant, declarations. Intellectually, Kekulé probably was Kolbe's superior, but not as a constructive worker. Frankland and Kolbe's synthesis of acetic acid (1846) is one of the most clear-cut achievements in the early history of the development of the doctrine of chemical structure: Kekulé seems never to have grasped its significance and the extent to which it put their work in advance of his."

My last talk with Armstrong before we reached Tangier was about the final episode in the battle of atomic weights, the Karlsruhe Conference.

In spite of the success of Gerhardt's classification among the younger chemists, the gradual realization of the combining powers of elements, and Kekulé's application of this idea in the theory of atom linking, chemistry in 1859 was still in chaos. There was no general agreement as to the basis of atomic weights or molecular magnitudes, and the various formulas proposed for acetic acid covered a page in Kekulé's *Lehrbuch*.

Kekulé saw that the acceptance of his theory of atomic linking depended on agreement about atomic weights, and in the autumn of 1859 he suggested to Weltzien, professor of chemistry at Karlsruhe, the idea of a chemical conference to discuss some of the fundamental issues that were in dispute. Weltzien met Kekulé and

Wurtz in Paris, and they sent a joint letter to their colleagues abroad asking their views as to the usefulness of such an international gathering. As a result an invitation went out from the organizers inviting them to a three-day conference at Karlsruhe on September 3, 1860. Over a hundred chemists came from almost every European country; Liebig, Wöhler, and Mitscherlich were absentees, but most of the active workers were present, so that the organizers must have hoped for great results. But there is a sentence in Gerhardt's treatise which proved only too true a forecast.

"What I do not understand is that when chemists meet for discussions, each speaking his own language, such discussions are always fruitless, even when the chemists are in complete agreement as to the facts—either because, without realizing it, each expresses the same facts in a language which his opponent does not understand or because they all give to formulæ a significance they cannot have, that of representing molecular structure."

Weltzien presided at the first session, and at Kekulé's suggestion a small committee with Hermann Kopp as chairman was nominated to draw up questions for discussion by the conference. This committee, like others, grew until it contained more than half the members of the conference, and its meetings took up much of the time. Cannizzaro at its first meeting proposed that Avogadro's hypothesis should be adopted as the basis for determining molecular size. This was not agreed, and at the second session the questions for discussion were:

1. Is it convenient to make a distinction between the terms "molecule" and "atom"?
2. Should the term "compound atom" be replaced by "radical" or "residue"?
3. The idea of equivalents is empirical and independent of the idea of atoms and molecules.

This session was presided over by Boussingault, a chemist of the older school, who did not give it a clear-cut lead by his opening remark that it was chemists and not chemistry that got out of

date. The discussion was abortive, and the questions were remitted back to the committee, which produced three new subjects for decision at the last session presided over by Dumas:

1. Is it desirable to make chemical notation conform to the progress of the science?
2. Is it convenient to adopt anew the notation of Berzelius with some necessary modifications?
3. Is it desirable to distinguish by special signs the new chemical symbols from those in use fifteen years ago?

Cannizzaro immediately rose to attack the second proposal. It was illogical, he said, to go back to Berzelius in view of the advance made by Gerhardt's classification and his formulas based on Avogadro. After a eulogy of Gerhardt he pointed out certain inconsistencies in his atomic weights which could be remedied with the help of specific heats and the law of isomorphism. Realizing, perhaps, that he was not carrying his audience with him, he ended with a compromise: "If we cannot agree to accept the new system, do not at any rate decide against it, as it is gaining supporters daily . . . and let us adopt the barred atoms to express the doubled atomic weights."

Cannizzaro's speech gained no supporters. Strecker pointed out that the name of Gerhardt had been replaced by that of Berzelius by a majority vote of the committee. Erdmann argued that the issue was not clear enough to take a vote on it. Odling with his usual clarity of mind insisted that at any rate they could agree that an element can have only one atomic weight. Speeches by Kopp, Erlenmeyer, Lothar Meyer, Boussingault, and Will were indecisive, and Kekulé said that decisions as to theory and nomenclature could not be made compulsory by a vote, but that the discussion had been useful. Dumas summed up in similar words, and the sole conclusion reached by the conference was that barred atoms should be used to indicate those atoms whose atomic weights had recently been doubled.

So the first international chemical conference broke up in a somewhat chilly mood without fulfilling the hopes of the organizers,

just as Gerhardt would have predicted. But it was not without results, for on the last day Pavesi had distributed a small pamphlet in a yellow cover, a reprint of a letter Cannizzaro had written to Luca in 1858 outlining a course of lectures in which he explained to his students the causes of the present uncertainties as to atomic and molecular weights. His exposition of the historical difficulties and their avoidance by the consistent use of the laws of Avogadro and Dulong and Petit was so clear and convincing that, as Lothar Meyer said, when he read it "the scales fell from my eyes, doubts disappeared and were replaced by a feeling of certainty." All the difficulties that had stood in the way of a general acceptance of Avogadro's law were resolved and the need of such relics of past controversies as the use of barred atoms disappeared. This made it possible for the theory of atomic linking to develop on a firm basis. However, it took some little time before all chemists accepted Cannizzaro's reformed atomic weights. Armstrong said that when he began to learn chemistry, two formulas for water, HO and H₂O, were still in use.

And this brings us to Armstrong's own training, which began in 1865, the year that saw the birth of the benzene ring, which was to absorb so much of Armstrong's thought and work. He "just slid into chemistry" under Frankland at the Royal College of Chemistry, and the story is best told in his own words. After four terms, "Frankland saw, I think, that to keep me at lessons was waste of time: at all events, he wanted someone to help him and paid me the compliment of asking me to work for him. . . . We were mainly concerned in devising methods for the determination of organic impurity in sewage and of sewage-matter in drinking waters. Frankland gave me only the barest instructions and left me to do the experimental work—the experience was invaluable: through it, at the age when I was only due conventionally to attend either Oxford or Cambridge, I became a confident, independent worker:

"I have always taken it as a high compliment and proof of his unselfishness that he advised me, in the summer of 1868, to go abroad and study under his old friend and companion at arms, Kolbe, then Professor at Leipzig."

Kolbe was "one of the most thorough and typical Germans of the old school it has been my good fortune to meet, a chemist who received but scant justice even from his own countrymen—few realise the extent to which he was the founder of our modern system of constitutional formulæ—because he dared to criticize and expressed himself in the biting terms of a clear and concise diction, in a pure German which no one else in those days had at his command: in fact, he took his countrymen greatly to task for their slovenly language. Of course, I was received with utmost cordiality. I well recollect how, on the afternoon of my arrival, Kolbe took me into his private laboratory and carried out with me the nitration of a quantity of phenolparasulphonate by means of sodium nitrate and sulphuric acid. He then suggested that I should take up the study of the mixture formed on sulphonating phenol. In those days we had not yet learnt even to distinguish three isomeric monoderivatives of benzene and phenol*orthosulphonic* acid was unrecognized. It was at this time that Kolbe began 'to slang' Kekulé over his benzene formula—I had not even heard of this before going to Germany. Such was my introduction to the "aromatics" and the beginning of my affection for sulphonic acids. . . .

"Kolbe's laboratory, in those days, afforded wonderful opportunities. About a dozen of us were doing advanced work, in preparation for the Degree—seeking independence. Each had his *Arbeit*—his definite problem—in view, as his chief aim in life: we were all proud of being called on to show that we could do something. This was the distinctive feature of the German system. At most two or three had themes from the Professor—the rest were carrying out ideas of their own; the work was, therefore, varied. Whatever suggestion we made to Kolbe, he never discouraged us; his habit was to grasp the lapels of his coat, then to reply: 'Try it, try it.' We disputed with him constantly before the blackboard, often for hours together, nearly always taking exception to his theoretical views—but without his being offended. And we constantly compared notes together. Each of us, therefore, was interested in the solution of a whole series of problems."

Armstrong stayed at Leipzig till 1870, and these years with Kolbe left their mark on him. From Frankland he had learnt

experimental technique, confidence in his power to attack a problem and the call of research. But Frankland was an individualist; he never founded a school, and as Armstrong said of him: "Frankland was so thrown upon himself, he so developed the art of self-help that he never learnt to order and use others sufficiently, which is the teacher's art; he kept counsel with himself." Frankland was a fine lecturer, but he disliked the routine of laboratory teaching.

Kolbe, on the other hand, was an outstanding teacher, and a great inspirer of research. In spite of his theoretical eccentricities, students flocked to his laboratory as they had previously gone to Liebig at Giessen. Armstrong owed to Kolbe his introduction to aromatic chemistry which came to be his most continuous and active scientific interest, and from him he learnt the value of that daily intercourse with students in the laboratory. Probably, too, his own provocative attitude toward easily accepted theories was influenced by Kolbe's hard hitting polemics.

Wherever Armstrong taught—at the London Institution, at the Finsbury Technical College, or at the City and Guilds Central College—his students were trained in method, they learnt to think for themselves. The result is seen in the unceasing flow of papers that came from his laboratory for half a century, inspired by him and representing the work of men who had the privilege of working side by side with him in the laboratory.

Although those papers contain no outstanding discovery, they covered many fields, and were a great contribution to our knowledge of the orientation of aromatic derivatives, the structure of the terpenes, the nature of enzyme action, and the morphological relations of the crystals of organic compounds. Armstrong always chose problems of real significance, but perhaps his greatest contribution was the stimulus he gave to his colleagues, his students, and his friends.

His mind was constantly ranging over a much wider field than chemistry, and while that may have diminished the intensity of his work on specialized subjects, it was the secret of his personality. I rather think that nature had meant him to be a biologist, as he had the eye and instincts of a naturalist, and a great love and understanding of living things; and he had too an intuitive perception of the things that matter to human life.

Armstrong was both a prophet and a pioneer. In so many directions he saw things ahead of his time, and having seen them, like his favourite writers, Ruskin and Carlyle, he lost no opportunity of preaching the gospel in trenchant phrases—the place of science in education, methods of teaching, the effect of diet on health, the value of fresh food, especially milk, the place of science in agriculture, the need for surveys of natural resources, fuel efficiency, and conservation. His utterances on all of them had the prescience that sets men's minds stirring long before the current of thought and knowledge has made things obvious. Christ's Hospital and Rothamsted were the larger laboratories where many of his ideas bore fruit.

In 1916, Armstrong was one of those who saw most clearly that when the war was over we had to face "a more enduring and difficult struggle in the fields of industry and commerce. The race will be neither to the swift nor the strong, so much as it will be to the intelligent and the persevering." He saw that coal was a key factor in our national economy. "At present our nation is without a coal conscience; get one it must without delay. In some way the public must be made to realise how absolutely coal touches our civilization at every point." Armstrong was a persistent and forceful advocate of the need for scientific method in the use of our national coal resources, and his was one of the voices that led to the formation of the Fuel Research Board in 1917. But it took yet another war to drive home the need for fuel efficiency that Armstrong saw so clearly thirty years ago.

Armstrong had both a very active brain and a pen that could keep pace with the rapidity of his thoughts, aided by wide reading and a responsive memory. All his occasional papers and addresses had such vigour and freshness and a character of their own. Today they are scattered and inaccessible, and a little volume of them would be a most fitting memorial to Armstrong's memory.

NOTES AND REFERENCES

- J. Vargas Eyre, "Henry Edward Armstrong," London, Butterworths Scientific Publications, 1958.
 Richard Willstätter, "Henry Edward Armstrong," *Nature*, vol. 120, 1 (1927).

From the First H. E. Armstrong Memorial Lecture, delivered before the Society of Chemical Industry at the Royal Institution on November 21, 1945, published in *Chem. & Ind.*, 50, 398-402, 406-410 (1945). This lecture, reprinted here with omission of a few paragraphs, includes biographical sketches of Auguste Laurent, 1807-1853; Carl Charles Friedrich Gerhardt, 1816-1856; Edward Frankland, 1825-1899; Hermann Kolbe, 1818-1884; and Friedrich August Kekulé, 1829-1896.

SIR HAROLD HARTLEY, F.R.S.

.. 63 ..

Henry Le Chatelier

1850-1936



IN MAY of 1934, it was the writer's privilege to present a certificate of honorary membership in the American Ceramic Society to Henry Le Chatelier at his residence, 75, rue Notre-Dame-des-Champs, Paris. Professor Le Chatelier had just returned from the Eleventh International Congress of Pure and Applied Chemistry in Madrid, where the honorary degree of Doctor of Science had been conferred upon him by the University of Madrid. Although he was in his eighty-fourth year, this tall, slender, white-haired scholar of France evidenced a clarity of mind which might have been the envy of a young man. While folding the diploma of the American Ceramic Society in the quaint old parlor, he reminisced about his earlier work. He was fully informed on the latest developments in the fields of chemistry, metallurgy, and glass technology. He had retired from active service, but held the title of Emeritus Minister of Mines of France, and still served as consultant to the ministry. Later, in the old garden with its giant trees, Professor and Madame Le Chatelier graciously posed for motion pictures. There was an ever-present look of mutual solicitude on the faces of this interesting old couple.

Henry Le Chatelier was born in Paris, on October 8, 1850. He was the son of Louis Le Chatelier (1815-1873) who was Inspector General of Mines for France. His father was one of the engineers who created the French National Railways, in whose interests he worked from 1855 to 1868. He was consulting engineer to bankers who financed the railway systems, not only of France, but also of Spain, Austria, and Russia. He was an associate of H. de Sainte-Claire Deville in the establishment of the first aluminum industry of France, and of Sir William Siemens with whom he constructed the first open hearth steel furnace.

His mother, Elisabeth Durand, came from a family of artists and scientists which included sculptors, engravers, and geographers. She was an ardent Catholic and through her own early environment and her love of poetry fostered in her son that appreciation of art and letters which was evident throughout his life.

His mother was a rigid disciplinarian and so directed the lives of her children that they would not only prove conscientious as students, but appreciate physical well-being and rest, as well. Henry arose early each morning and prepared his lessons. Later, on entering the École Polytechnique (1869), he would go to his father's study each morning at 7:30 and review his lessons for the day. He learned to respect law and order, and he enjoyed the almost military attitude in the École Polytechnique. Even his grandfather was a factor in determining Henry's career. He operated lime kilns, and during his vacations Henry would visit his grandfather's plants where he acquired his first interest in mortars and cements.

While Henry was at the École Polytechnique he assisted his father and, as the latter received visitors who were interested in the fields of agriculture, medicine, chemistry, and metallurgy, the son gained valuable experience. To observe the analytical mind of his father and the manner in which he solved problems was helpful. Not only would the father teach him mathematics, but he would provide him with essays on chemistry which had been written by Sainte-Claire Deville, Debray, Dumas, Chevreul, and others of his associates. The boy read the reports of the French Academy of Sciences. He was permitted to assist his father when the latter helped create the aluminum industry, and thus gained much first-hand information about this new metal. Sainte-Claire Deville permitted the lad to work in his laboratory and cooperated with the father in guiding the son's efforts. Henry Le Chatelier stated many years later that the influence of his father and the contacts with his father's associates were important influences in "shaping his career and establishing that reputation which he held as a chemist."

While we are considering his father, mother, grandfather, and others who influenced Henry's career, it might be interesting to note that his own brothers and sister were also interested in science. His brother Louis was a bridge and railway engineer, and constructed steel plants. Alfred was an army officer and had much to do with the development of the French colonial empire. This brother worked on high temperature enamels. His brother George was an architect. A fourth brother, André, the oldest of the children, worked with Henry in creating the autogenous welding in-

dustry and devised methods for the safe storing of liquid acetylene. He studied the resistance of metals to high temperatures, and devised metal lath, which is still in use. This substitute for wood possessed a much greater strength and was fireproof. The sister, Marie, married a Dr. Leroux who was a pediatrician.

Henry's early education was obtained in Paris where he attended a military academy for a short time and then entered the Collège Rollin, receiving the Bachelor of Letters in 1867 and Bachelor of Science in 1868. He entered the École Polytechnique in 1869 but his work was interrupted by the War of 1870. His studies were completed in 1872, and he registered as a mining engineer. In 1874 he was licensed to practice physical science. In 1877 he became professor in the École des Mines. In 1882 he was lecturer in the École Polytechnique. In 1883 he became professor in the Collège de France and later professor at the Sorbonne. The degree of Doctor of Physical and Chemical Science was conferred upon him in 1887, when he became professor of industrial chemistry and metallurgy in the École des Mines. Until 1897 he devoted himself to the mechanics of chemical reactions, establishing the laws of chemical equilibrium and the displacement of equilibrium. He studied solutions. By applying thermodynamic values he was able to anticipate possibilities, instead of depending on trial-and-error methods and performing costly experiments with possible negative results. In 1889 he won the title of chief engineer and that year returned to the Collège de France as professor of inorganic chemistry, remaining until 1908. In 1907 he had been appointed professor of general chemistry of the Faculty of Science of Paris—a title he retained until he became honorary professor in 1925. During the period 1908 to 1922 he directed the researches of more than one hundred graduate students, of whom twenty-four obtained the doctorate as his majors.

Le Chatelier was a reformer. He was not content with providing the descriptive material and facts which his colleagues presented, but constantly introduced theory and the newer ideas, presenting his own interpretation of fundamental principles and laws.

In the research field Henry Le Chatelier possessed great versatility. He is recognized chiefly for his contributions to thermodynamics and chemical theory. We are familiar with his principle

on stress and strain, which is coupled with that on heat advanced by van't Hoff. It is not strange that he should have accomplished the synthesis of ammonia from the elements in 1901, anticipating Fritz Haber, who is usually the only one mentioned in connection with the process. Henry Le Chatelier was interested in allotropy, especially in carbon, silica, and certain metals. He made extensive solubility studies, including dissociation. He studied the dissociation of gases at high temperatures and the combustion of gas mixtures, and applied the results to the utilization of fuels and the economics of furnace operation. Later he entered the field of explosives and indicated their use in mining operations. While generally interested in metallurgy, he devoted himself more particularly to the production and properties of iron and steel. He applied the phase rule of Willard Gibbs for which he devised simple proofs, and it is said that without Le Chatelier's principle of mobile equilibrium the phase rule and phase law diagrams might have waited long for their practical applications. While working in the field of metallurgy he devised a metallurographic microscope with which he could study and photograph crystals in alloys. This device divulged the formation of compounds between iron and carbon, and proved the value of heat treatment in steel. His dilatometer enabled him to measure the expansion rate of metals. Le Chatelier experienced difficulty in the measuring of the higher temperatures in his studies. Instruments were in existence which would measure up to 500°C ., but beyond that results were inaccurate. He adopted the platinum-platinum-rhodium thermocouple, for gas thermometers were unreliable.

In the field of ceramics Le Chatelier was interested in mortars and cements, clay, silica, glass, and the silicates. He determined the coefficient of expansion and electrical conductivity of some of these materials.

Henry Le Chatelier published over five hundred journal articles and books. They included chemistry, ceramics, numerous biographies, and, toward the end of his life, articles on social welfare.

Le Chatelier's books included a volume on the measurement of high temperatures which appeared in 1900 under the joint authorship of O. Boudouard. This volume underwent numerous revisions

and translations, and is known in the United States under the title, "The Measurement of High Temperatures," by Burgess and Le Chatelier. In 1903 a volume appeared on "Hydraulic Materials." This dealt with lime, mortars, and cement. Again, the volume was revised and translated. In 1908 he published his "Lessons on Carbon." This volume had its beginning in his early lectures on the subject. The year 1912 brought his "Introduction to the Study of Metallurgy" which included industrial heating. In 1914 his volume on "Silica and the Silicates" appeared, and in 1925 his book on "Science and Industry." In the last-named volume he particularly stressed the Taylor system of organized management and production which originated in England and which he greatly admired.

In his books and journal articles Le Chatelier's exact scientific trend of mind is in constant evidence. He provides illustrations, but sparingly, and never superfluously. His translators were more generous in this regard than the author himself.

Le Chatelier was a great national figure. His linking of science with industry (especially with national defense) was important to France, for not only the nation but the Academy of Sciences had neglected this. His frequent appeals to the French Academy of Sciences, in which he referred to the utilization of science in industry and national affairs in Germany, Great Britain, and the United States finally won national support for research, and his favorable reference to our own nation undoubtedly prompted Woodrow Wilson to consult him in an advisory capacity when our National Research Council was established in 1916.

The reward of Le Chatelier's appeal to the National Academy of Sciences and the French nation came through his numerous appointments. He was on the French Commission on Explosives in 1902, the National Science Bureau in 1913, the Commission on Weights and Measures from 1913 to 1917, and the Commission for the Standardization of Metallic Products. Upon him was placed the responsibility for specifying standards for materials of construction other than wood, and his committee finally determined the standards for all products. In 1919 France made him a member of the Commission on Inventions, and in 1922 he was

placed on the Committee for the Control of the French Monetary Circulation. Le Chatelier represented France at numerous international meetings.

Henry Le Chatelier was the recipient of many honors. These included the Jerome Ponti Prize of the French Academy of Sciences (1892), and the Lacaze Prize (1895). In 1907 he was made a member of the French Academy of Sciences. It may seem strange that the Academy should have waited so long, but one has only to think of the case of Louis Pasteur to realize that election to this body requires time. He had been a Chevalier of the Legion of Honor of France since 1886. In 1908 he became an officer, in 1919 a Commander, and in 1927 Grand Officer. In 1906 he was made a knight of the Order of St. Anne of Russia, and in 1928 a Chevalier of the Order of the New Republic of Poland.

His applications of science to industry brought him recognition which scientists rarely receive. Thus, in 1900 he received the Grand Prize of the Paris Exposition; in 1908 the Medal of Honor of the Society of Mineral Industry of France; in 1928, the Gold Medal of the Commission on Bridges and Highways of France. In 1904 he received the Grand Prize of the St. Louis Exposition (U. S. A.); in 1905 the Diploma of Honor of the International Exposition in Liège, Belgium; in 1906 the Grand Prize of the International Exposition in Milan, Italy. During 1910 he received the Grand Prize of the International Exposition in Brussels, Belgium; the Grand Prize of the Franco-British Exposition; and the Bessemer Gold Medal of the Iron and Steel Institute of London. In 1911 the International Exposition of Industries and Manufacturers of Turin, Italy, awarded him the Grand Prize. In 1916 he received the Davy Medal of the Royal Society of London. In 1932 he was awarded the medal of the Association of Engineers of Liège, Belgium. Henry Le Chatelier was not only a member and officer in many national and foreign societies, but was made an honorary member of innumerable organizations.

Le Chatelier's honorary degrees included that of Doctor of Engineering from Aix la Chapelle, Germany (1910); Doctor of Science from the University of Manchester, England (1920); Doctor of Technical Science from the Polytechnique Institute of Copenhagen, Denmark (1921); Doctor of Science, University of Louvain, Bel-

gium (1927); Doctor of Science, University of Madrid, Spain (1934).

It would hardly seem right to present this chapter without saying something of Le Chatelier's family life. On May 29, 1876, he married Genevieve Nicolas, the daughter of a former chum of his father at the École Polytechnique. There were seven children by this marriage, three sons and four daughters. The influence which Henry Le Chatelier enjoyed through his grandfather, his father, and mother, and their families is repeated through his influence and that of Mme. Le Chatelier on their children and grandchildren. The oldest son, Charles, became a mining engineer. The oldest daughter married an engineer. The next daughter also married an engineer and after her marriage cooperated with her father in establishing the *Revue de métallurgie*. The third daughter married an agricultural engineer. The son, Louis, is an engineer. The fourth daughter married an engineer, and the youngest child, a son, François, is a mining engineer. It is to this son that the writer is particularly obligated for much of the valuable information contained in the present article.

In June, 1936, Professor and Mme. Le Chatelier celebrated their sixtieth wedding anniversary surrounded by their children, thirty-four grandchildren, and six-great-grandchildren. Le Chatelier devoted all of his spare time to his family. The tall, slender, serious, but pleasant, father played with the children and would take them on numerous excursions. He interested himself in their studies and in the studies of his grandchildren. It is said that in the spring of 1936 he went to Miribel-les-échelles with his grandchildren to give them a review in chemistry and physics, and that on the eve of his death, disregarding his fatigue, he dictated to one of his children advice concerning the study of descriptive geometry to help a grandchild who was experiencing difficulty with the subject.

We must pay tribute to Mme. Le Chatelier. Her self-abnegation as the wife of a professor with a limited income, and her devotion to the education of her children to lighten the burdens of her husband as much as possible proved an important factor in helping to establish his brilliant career.

Le Chatelier traveled extensively in the interests of his studies

and through invitation of foreign societies; also during his vacation, when Mme. Le Chatelier invariably accompanied him.

Finally, like most scientists who reach a ripe old age, he indulged in philosophy. On January 22, 1922, the French Academy of Sciences celebrated the fiftieth anniversary of Le Chatelier's graduation from the École Polytechnique and presented him with a bronze medal. Copies of this medal by an eminent sculptor had been distributed in return for subscriptions resulting in a fund of 100,000 francs. This fund was presented to the Academy of Sciences in Le Chatelier's honor and utilized for researches under his direction. There were many addresses in which he was given high praise and commendation. When his friends and associates had finished Le Chatelier thanked them and closed by stressing some of his own ideals. He emphasized the necessity for clear thinking verified by exact experimentation, and illustrated the importance of this procedure by citing the failures of a number of eminent men whose carelessness resulted in embarrassment following their published accounts of faulty researches. He told how his pleasure in life had come through studying the laws of the universe, observing their application and discovering new consequences. He warned against the tendency to invalidate or question natural laws and said that one should aim to confirm those laws which predecessors had disclosed. He felt that this attitude was an advantage which led to his own supplementary contributions and which accounted for that measure of his success which the Academy was celebrating. He could not destroy the edifices of the past, for he considered science "a collection of contributions made by many workers, which might be supplemented or modified by duly authenticated new discoveries." He stressed the importance of discipline which his parents had imposed upon him and which was practiced at the École Polytechnique while he was a student. He deplored the decreasing seriousness of study and increasing tendency toward pleasure and even license in modern colleges and universities. He likened the irresponsible student to a bold individual who dodges vehicles in crossing a street and risks being crushed, to say nothing of the fact that he seriously ties up traffic. To the young chemist he recommended modesty coupled with a reluctance to overthrow the findings of the past until he has posi-

tive proof. "One makes discoveries if he can and not merely through the wish to make them. The sensational is detestable." Of himself Le Chatelier said, ". . . throughout my scientific career I strove without any desire for the sensational, contenting myself each day with the conscientious pursuit of the task of the day. In the end I was amply rewarded."

Le Chatelier was a lover of liberty and cherished the privileges which men enjoyed in the French Republic. He differentiated between discipline and liberty. To him discipline meant the voluntary respect of the law, whether natural or social. He characterized civilized man through recognition and respect of the law. To him liberty consisted not in the breaking of laws, but, on the contrary, in the prevention of law violation. Liberty refuses to tolerate injustice and should modify laws instead of revolting against them.

Le Chatelier placed integrity above everything. At one time after he had received an honor, a statesman approached him for a favor to a particular political faction. Le Chatelier replied, "I have never sought an honor, and I, therefore, assume that when it was conferred it was mine without obligation." He might have enjoyed favors and promotions had it not been for this ideal. In fact, he lost his chair in the École Polytechnique through his conscientious adherence to his principles.

After his retirement and during the last years of his life, he became interested in numerous problems of a general nature. He campaigned for the return of the classical studies to college and university curricula, stressing the importance of literature and Latin as a part of a general education. As already intimated, he advocated scientific management according to the Taylor System, and others, for increasing the efficiency of workmen in French factories. He advocated political economy, recommending a more liberal status for the workman and a greater restraint on political expenditures. Shortly before his death, as president of the inaugural International Congress of Mines and Metallurgy and of Applied Geology, at which delegates from forty nations were present, Le Chatelier took occasion to indicate that much attention was being given to the development of industrial technique which was based on the collaboration of science and industry. He admitted that at one time he had supported this policy and that it was still

desirable, but lamented the fact that not enough attention was being paid to social progress. Wishing to leave this thought as an indelible impression, he prepared an article entitled "Morals and Human Affairs." So anxious was he that the manuscript should be exactly right, that he corrected it on his deathbed, and insisted repeatedly that it be sent to a journal where the ideals expressed would make a sympathetic appeal, namely, the *Bulletin of the Social Union of Catholic Engineers of France*. It appeared in this *Bulletin* as a posthumous article in December, 1936.

After 1935 Le Chatelier suffered occasionally from angina pectoris. Several days before his death a particularly violent attack affected his heart, and he succumbed. His death was a peaceful one, on September 17, 1936, at his country estate, *Miribel-les-échelles* (Isère), France, in his eighty-sixth year. The writer pays tribute to Henry Le Chatelier, one of the world's greatest scientists, in a poem which was previously prepared for a memorial article.

Father studied of Earth's minerals,
 Father's father burnt its lime,
 Mother's forebears mapped world nations,
 She herself was soul sublime.

Thus, the son, one born of Genius,
 Nurtured by the mother's care,
 Guided by the father's wisdom,
 Must find interest everywhere.

And he did, in Natural Science,
 Striving morning, noon and night,
 Wrest from Earth some of her secrets,
 Set them forth, as well he might.

First the gross, the coarser findings,
 Then with microscope, the small,
 Next the laws, their explanation
 Gave this Savant, slim and tall,

Always striving, earnest, modest,
 More to learn and more to give.
 Discipline, his life, his motto,
 Showing others how to live.

Not for pleasure, not for glamour
But to serve both Man and State,
In this service helped a woman,
That self-sacrificing mate,

Who with patience him encouraged,
Bore him sons and daughters rare.
These love art and science also,
Further lay Earth's secrets bare.

Nations far and wide our Scholar
Honored in their Guilds, and then
Made him of their Groups a member;
Always happy, where and when

He would visit, in his travels,
Their great scholars, more to learn;
Learn, but giving more than taking,
Adding to Minerva's urn.

Flames he measured, as to hotness,
Even solar heat, so high,
Glasses made he in the furnace,
Products pleasing to the eye.

But his sunset saw the smoulder
In his fellow worker's breast,
Which portraying surface under
Showed a feeling of unrest.

Showed that some had blessings many,
Others few. These torn with strife
Often suffered untold tortures,
Trudging through the walk of Life.

Thus, on death-bed, leaving Science,
He espoused the Public Weal,
Pleading strong the Cause of Justice,
Signing with his last Earth-Seal.

May his message bear fruition,
Lift from Life its shaded hood,
Make men see that Life's worth living,
Holding hope, and boding good.

Gone our Savant. Yes, in body;
Not in mind or soul, for they

Will abide with us forever.
They'll live Aeons, no mere days.

NOTES AND REFERENCES

This chapter was compiled from a number of articles on Henry Le Chatelier, written by the author and published in 1937:

"Henry Le Chatelier: I, His Life and Work," *Bul. Am. Ceram. Soc.*, 16, 155-163 (1937).

"Henry Le Chatelier: II, His Publications," *J. Am. Ceram. Soc.*, 20, 316-322 (1937).

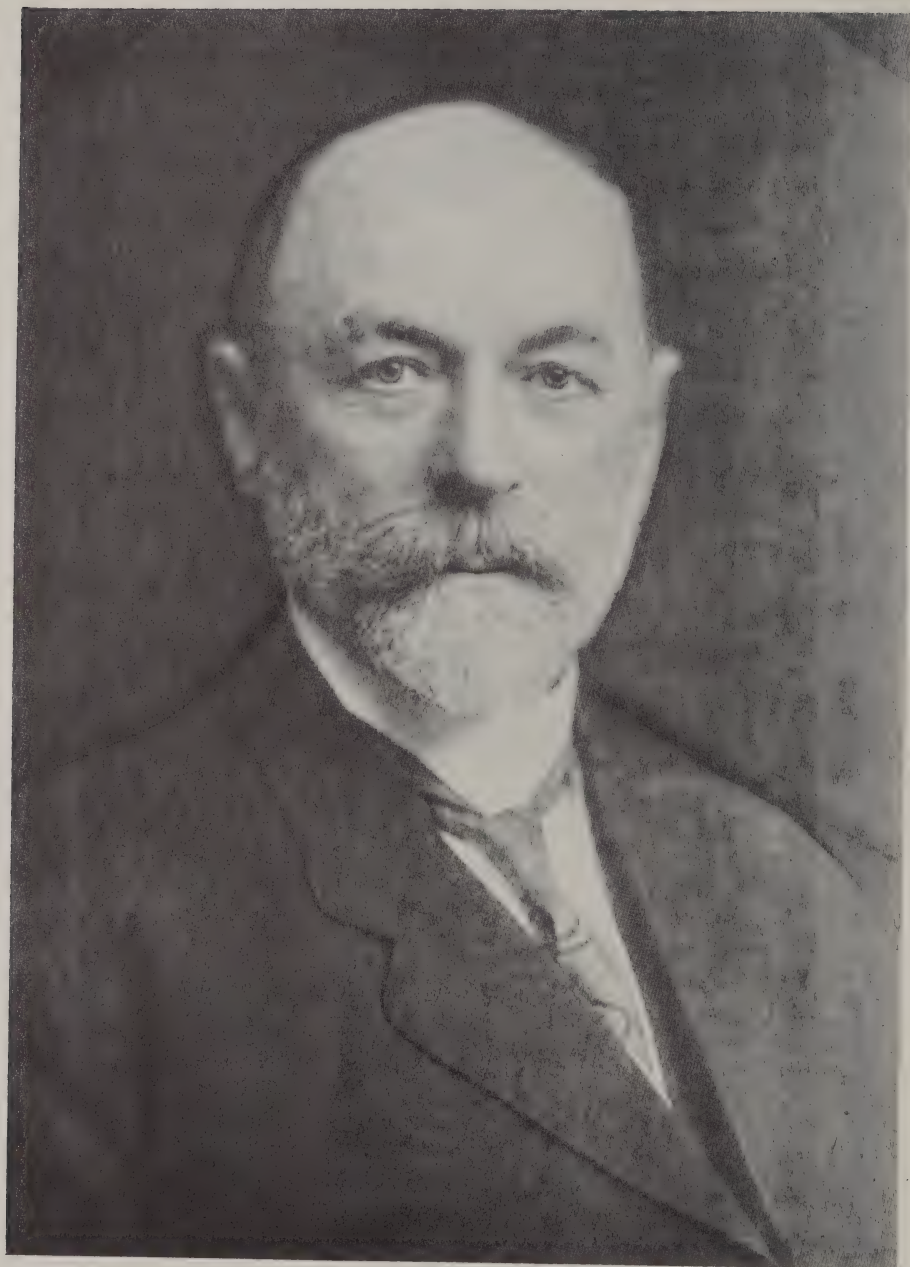
"Henry Le Chatelier: 1850 to 1936," *J. Chem. Educ.*, 14, 555-560 (1937).

ALEXANDER SILVERMAN

.. 64 ..

Herman Frasch

1851-1914



HERMAN FRASCH performed his great experiment in a 10 inch test tube 625 feet long. His laboratory was an island in the middle of a Louisiana swamp, a 75 acre oasis of dry ground, studded with giant cypress, all festooned with Spanish moss, and inhabited by muskrats, a colony of snowy egrets, and mosquitoes, billions of mosquitoes. Scarcely ideal experimental conditions, these, but in no other way could he find out whether his idea would work or not. A number of experts had told him bluntly that it would not; that he was crazy to think he could melt sulfur underground and pump it to the surface in molten form.

Yet his revolutionary idea was fundamentally quite simple. He had hit upon it because of his long experience with petroleum drilling and with pumping brine out of driven wells. All the equipment he proposed to use was as simple and standardized as a foot rule. Furthermore, Frasch was not only an able chemist, he was also a meticulous, forehanded engineer. At his desk he had carefully calculated all the factors involved; temperatures, pressures, thermal efficiencies, and specific gravities. But he could not check these figures by laboratory experiments. He could not even test them in a pilot plant. He was compelled to leap from paper calculations to field operation. The whole thing had to be a gigantic gamble.

It required courage to take such a long chance. Frasch never lacked self-confidence: at times he displayed an unblushing, almost brassy assurance. Even his warmest admirers had to admit that he was "opinionated," but his opinions were always well buttressed with facts and figures. He knew what he was talking about. He never went off half-cocked. Accordingly, his great sulfur gamble was really a carefully calculated risk, and he was confident of success. He could not have foreseen all the problems and disappointments ahead nor suspected the persistence and resourcefulness that would be demanded of him. If Frasch had not been a

remarkable man with a surprising assortment of gifts and skills, he would never have perfected his hot-water sulfur mining process. But it would never have been a commercial success, if he had not also been very lucky.

Some 500 feet beneath his island-laboratory lay a 100 foot stratum of limestone richly impregnated with sulfur. The structure seemed to be quite like the famous deposits in Sicily which, since Roman times, had been the world's chief source of brimstone. Following the close of the Civil War, forty years before, a dozen attempts to reach this buried treasure had failed. The insuperable difficulty was a layer of quicksand from which, when dug into, flowed a fountain of salt water charged with poisonous hydrogen sulfide gas.

The sulfur mine that could not be mined became notorious. It was thoroughly explored by core-drilling. Geologists wrote reports about it that were published in learned professional journals. At least three consulting mining engineers risked their reputations by suggesting novel, but impractical, methods of penetrating the tricky, dangerous quicksands. A lot of money was lost, some of it by gullible investors in companies that were little better than get-rich-quick schemes.

The final effort to mine this baffling deposit was made in 1890 by Abram Hewitt and his brother-in-law, Edward Cooper, a partnership that combined ample venture capital with successful mining experience. Their American Sulphur Company bought the sulfur island outright, and they planned to tunnel through the quicksand within a series of iron rings, 10 feet in diameter, lowered to the bottom of an old shaft and welded on top of each other till the last ring stood above the surface of the ground. As the men dug out the clay and gravel at the bottom of the shaft, the weight of the rings forced the improvised caisson lower and lower. All went well till they struck the quicksand. In surged a mixture of sand and water that carried the pump platform and workmen 40 feet up the shaft. With a clamshell bucket they scooped out the sand till the shield had been lowered the depth of four more iron rings, about 20 feet. Not an inch further would it budge.

Tragedy capped this failure. In one of their test wells the pipe

had broken 25 feet below the surface and in attempting to salvage it five men were asphyxiated by a sudden gush of deadly hydrogen sulfide gas. This fatal accident persuaded Hewitt and Cooper to abandon their ill-starred venture.

How Herman Frasch first became interested in this thwarting sulfur mine is not known but, being Frasch, he investigated it scrupulously. He admitted having read all the literature, including the highly imaginative circulars of the stock promoters. Nobody else interested in this frustrating project had thought to do so, but he studied the world market for sulfur and the business of the powerful Sicilian monopoly. He reached a crucial conclusion: even if it were possible to reach this rich deposit, it could not be mined profitably by pick and shovel. Labor costs would be prohibitive. Sicilian miners were then being paid 30 cents a day; Americans, \$1 to \$1.25—and the Sicilian workday was two hours longer. Accordingly, he decided to devise an entirely new method.

Frasch had a gift for attacking familiar problems from a fresh point of view. Thus he excelled in improving old chemical processes by what appeared to be sensationally original, unorthodox means, and his hot-water mining process, while highly original, was a synthesis of ideas developed naturally by his training and experience.

He had his first schooling in chemistry in Germany, for he was born on Christmas Day, 1851, at Gaildorf, Württemberg, and did not come to the United States until he was seventeen years old. After finishing in the local school, his father, Johannes Frasch, prosperous apothecary and mayor of the town, sent him to the gymnasium at Halle. He was anxious that his son proceed to the University, but young Herman itched to get to America. He landed at Philadelphia and immediately got a position at the Philadelphia College of Pharmacy as assistant to the distinguished Professor John M. Maisch.

Arriving in 1868, amid the first burst of industrial expansion that followed the Civil War, Frasch seems to have sensed the growing importance of chemicals and the opportunities opening up to chemists. At all events, he continued his chemical studies enthusiastically. Pennsylvania petroleum was booming and astutely

he began to investigate this complex mixture of hydrocarbons, becoming one of the first and foremost specialists in this new field.

He continued teaching and built up a little consulting practice till 1877 when a patent was issued to him for an improved process for refining paraffin wax. This he sold to the Merian & Morgan Paraffin Company, in which John D. Rockefeller's Standard Oil Company held a substantial interest. Assured by an annual retainer fee from J. B. Merian and William Morgan, he moved to Cleveland, opened an office and small laboratory, and became known as "The Flying Dutchman" with the reputation of being the outstanding chemical consultant in the city, then a hotbed of petroleum activities.

The oil recently found in Ontario attracted his attention. Its high sulfur content gave it an evil odor—it was nicknamed "skunk oil"—and the kerosene refined from it, then the principal petroleum product, burned badly, coating the lamp chimney with soot and gumming up the wick. In 1882 he sold "exclusive use of three patents" for improvements in refining Canadian crude to the Imperial Oil Company, Ltd., for cash and stock, and in 1884 he moved to London, Ontario. The following year he bought the Empire Oil Company which had wells and a small refinery at Petrolia, Ontario. Despite a protective tariff of 9 cents a gallon,

HERMAN FRASCH.

FABRICANTEN VON:

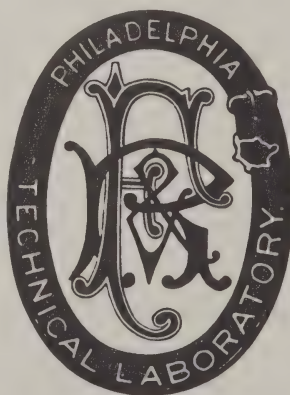
Brauermaterialien,

Bierschöne, und allen in das
Brauerfach einschlagenden
Chemicalien.

Saure Biere wieder hergestellt,
und Auskunft ertheilt in allen
Fällen in denen chemische
Hülfe von Nutzen
sein kann.

OFFICE:

No. 716 RACE STREET.



JOHN RUEGENBERG.

FABRICANTEN VON:

Künstlichen Fruchtesencen,

Brandy, Whiskey,
Gin, Rum, und Wine flavors.

Beste Weinschöne, ohne Geruch
oder Geschmack, ist unfehlbar.

Bittersmischungen feinsten
Art nach Verlangen.

Kranke Weine restaurirt.

LABORATORY: LANCASTER AVE.

Above Forty-fifth Street.

this struggling firm was almost bankrupt, but Frasch believed he could rescue it by making its products profitably salable. He had not completely solved these problems when, in August, 1886, he was called back to Cleveland by John D. Rockefeller.

A similar sour petroleum had been discovered in northwest Ohio and northeast Indiana, the famous Lima field. Although it was only salable as an industrial fuel, the Standard Oil Company and various subsidiaries, to maintain their dominating position in the industry, had not only bought many wells in this new area, but were taking in oil at 5 cents a barrel from independent producers. Their problem was becoming acute: they were storing skunk oil much faster than they could market it. As the best authority on this unmanageable crude, Rockefeller turned to Frasch; he gave him Standard Oil stock for his Empire property, bought his patents relating to the refining of sour oil, engaged him as a full-time consultant, and sent him to the brand-new Solar Refinery at Lima in charge of the first experimental research program ever undertaken in the American petroleum industry.

Frasch adopted a simple concept for the removal of the offending sulfur, based upon the reaction between a metallic oxide and the sulfur compounds in the oil, forming a sulfide which could be precipitated and from which the metallic oxide could be subsequently recovered for reuse. His basic patent, issued February 21, 1887 (U. S. Patent 378,240), covered the use of the oxides of copper, lead, iron, bismuth, cadmium, mercury, and/or silver in all possible combinations. From the start his process was an improvement over the old litharge treatment, but it took him the better part of two years to find the answers to such questions as (a) Which oxide or combination of oxides and in what proportions would do the best job cheapest? (b) Should the sulfur be precipitated in the first distillation or in the redistillation to separate the kerosene? (c) What type of agitation would insure the optimum formation of sulfides? (d) How best to recover and revivify the oxides?

The successful outcome of "Herman's Experiment," as the oilmen christened the Lima refinery, had far-reaching results. When the "last word" in petroleum refineries was built at Whiting, In-

diana, elaborate research facilities were provided and one of his assistants, Dr. William M. Burton, fresh from Johns Hopkins and later to perfect the cracking process, was installed as director. When the even greater refinery was built at Bayonne, New Jersey, larger laboratories were installed and the same policy of continuous research was adopted. Between 1899 and 1905, Frasch was assigned to Bayonne as special consultant on a part-time basis with a salary of \$8000 a year, and here he studied the Beaumont and Coalinga crudes and developed the recovery of by-products from the "slops" from the Atlantic Refinery at Franklin, Pennsylvania. Here, too, he urged the adoption of metal baffles in the fractionating towers in place of the stone packing used in the Van Dyke towers. Had his idea been approved, it might well have brought the bubble tower into refinery technique fifteen years sooner. It is recognized that Frasch was the father of research in the petroleum industry.

A more immediate, direct result of his own researches was that Lima crude, when properly desulfurized, advanced in price from 14 cents to \$1 a barrel. For his Empire Company and his stock in Imperial, Frasch had received Standard Oil stock paying 7 per cent dividends and selling for \$168 a share. The enhanced value of the sour mid-continent oils, in which the company had a commanding position, raised the dividend to 40 per cent and Frasch sold half of his stock for \$820 a share. He was now independently wealthy. He refused a regular executive post, but accepted a lifetime contract as part-time consultant with Standard Oil. He insisted that always, every year, he should have at least two sabbatical months of his own choosing.

Frasch had just perfected a new method of recovering the sulfuric acid used in refining the heavy fractions of crude oil, when he received his first patents (U. S. Patents 461,429 and 461,430) on his sulfur-mining process. Two Standard Oil officials, Frank Rockefeller and F. B. Squires, who had been closely associated with him in the Solar refinery experiments, became interested in this rather fantastic project and Frasch assigned to each a three-tenths interest in these and all future sulfur-mining patents. The three agreed to share, in proportion to their respective patent ownership, the expenses of development work. This was to

be conducted as a majority of the partners directed and to continue as long as a majority believed it promised success. If the project materialized, a corporation would be formed to take over and exploit the patents and to secure any property that had been acquired by the group.

It was under this agreement that Frasch went wildcatting for sulfur in the vicinity of the now-abandoned mine of the American Sulphur Company. He had been misled by his preliminary studies into thinking that the Louisiana deposit, like those in Sicily, extended underground over a large area. Four exploratory wells, each drilled 1000 feet through nothing but the typical sedimentary deposits of the Gulf Coast region, convinced him that all the sulfur in this neighborhood was beneath that island in the swamp, concentrated in the cap rock of a salt dome. These curious structures, described as "a billiard cue of salt, tipped with a limestone cap rock" are found in many parts of the world. But only along the Gulf Coast, between the delta of the Mississippi and the peninsula of Yucatan, is the cap rock loaded with sulfur. And only from the cap rock of a salt dome can sulfur be mined by the hot-water process.

With his partners' consent, Frasch went to Hewitt, and after some brisk negotiating, they came to an agreement. If he, at his expense, could produce sulfur, then a company would be organized in which each party would own half the stock—a fifty-fifty deal; the Cleveland group's patents and American Sulphur's property.

Frasch moved his drilling rig and expert crew over to the island and started a 10 inch bore. The infamous quicksand gripped the drilling bit as in a vise and it took three months to reach the limestone stratum, a job modern drilling tools could do in a day. Into the cap rock they firmly set the bottom of a 10-inch pipe, reduced the size of the bit, and continued an 8-inch bore through the sulfur bed. While drilling through this stratum a fountain of sulfurous water flowed continuously from the top of the drive pipe and they had to raise the rig eight feet high on a platform to be clear of the choking, smarting, dangerous gases. The men called it "the headache post."

The bore through the sulfur deposit was fitted with a 6-inch pipe

at the bottom of which was a perforated section to act as a strainer. Above the strainer, in the 6-inch pipe, was an iron ring with a hole $2\frac{1}{2}$ inches in diameter, and above the ring were larger holes in the pipe to provide for the hot water outlet. A 3 inch pipe was now lowered through the 6 inch casing and set upon the iron ring above the strainer. At 175 feet below the surface, an ordinary oil well sucker-rod pump was placed in the 3 inch pipe. At the top of this pipe was a tee which carried a pipe, fitted with a safety valve, beyond the wellhead. The gigantic test tube was now all set, ready for the experiment.

Frasch came down from Cleveland after Christmas, 1894, and he checked the steam and water lines himself. Superheated water was poured down the 6 inch pipe for twenty-four hours. Frasch opened the safety valve. A jet of steam burst forth which soon subsided and then ceased. Evidently the bottom of the well had sealed over with melted sulfur, so the sucker rod was set and the pump started. For four hours a molasses-colored stream of molten sulfur poured forth. Then the pump faltered and stopped. The steel sucker rod, corroded down to a matchstick, had snapped.

The Frasch process had brought to the surface liquid sulfur that solidified in minutes to sparkling yellow brimstone, better than 99.5 per cent pure elemental sulfur. But it was still far from a practical operation.

Twice the sucker rod broke, and Frasch, typically, cured this fault by eliminating the pump altogether and substituting compressed air. The sulfur froze in the pipe, which had to be pulled, disjointed, and over 400 feet chipped clean with cold chisels. In some wells the hot water drained away ineffectively through fissures. In others, where the limestone structure was exceptionally tight, it backed up and bleed wells had to be drilled to carry it away. When the sulfur melted out, the limestone collapsed, creating a new set of problems.

Working blindfolded, 600 feet down, it took Frasch six years to achieve commercial production. Luckily, the Louisiana dome was shallow, extraordinarily regular in formation, and comparatively easy to work. Otherwise the Frasch process might never have been perfected.

Having learned to mine sulfur efficiently, Frasch could not sell it profitably. The prime requisite of his process is millions of gallons of clean water: the prime cost is fuel. It took 4000 gallons of water, heated to 230°F. to raise a ton of sulfur. Water was plentiful; but the cheapest fuel was soft coal costing \$4.05 a ton delivered. Again it was very lucky that, just as he had ironed the kinks out of his operation, the greatest gusher in all petroleum history was brought in only thirty miles away. Fuel oil at 60 cents a barrel, piped over from Spindletop, made the Union Sulphur Company (the 50-50 corporation that had been formed by Frasch and Hewitt) a financial success.

As a businessman, Herman Frasch displayed the same boldness, skill, and resourcefulness that characterized him as a chemist. He had to fight his way into the market and he audaciously invaded Europe, breaking the grip of the Sicilian monopoly in their oldest strongholds. So long as his basic patents were in force, the Union Sulphur Company had virtually a monopoly in this country, but he lowered the domestic price drastically. He realized that the cheaper sulfur was sold, the wider and greater would be its consumption, and he preferred to build for the future than to make an immediate killing. Recognizing that his biggest customers were acid makers buying an essential raw material and, as such, most interested in a known, staple price, he adopted the policy of selling sulfur only in carloads, f.o.b. mine, at a price openly quoted to all. He initiated and paid for research to remove the fire and explosion hazards from grinding brimstone. He himself worked on improvements in the design of sulfur burners for the manufacturers of sulfuric acid. Union Sulphur was one of the first American companies to enter into cooperative research with state agricultural experimental stations and it supported liberally studies on sulfur as a fungicide and insecticide. At the turn of the century, all this was managerial thinking far in advance of the times.

For the future of the Union Sulphur Company Frasch died at a critical period. After a long illness he passed away in Paris, May 1, 1914; three months before the Kaiser's armies invaded Belgium; five months before a second American company, using his hot-water method, pumped sulfur from a dome in Texas. He could not

have foreseen World War I, but in anticipation of the new competition he was building up a huge stockpile of brimstone. This proved to be of inestimable value in meeting the war demands but, on the other hand, these demands enabled the new company to establish itself firmly.

By the time hostilities ended the sulfur situation had changed completely. Union Sulphur had lost its patent infringement suit and the hot-water process was thus thrown open to anyone. A third strong company had just come into production. Union Sulphur's own dome in Louisiana was beginning to show unmistakable signs of exhaustion. The company Frasch founded gradually faded away, but the American industry based upon his ingenious process had already become the chief supplier of "the most important chemical raw material."

Herman Frasch was awarded the Perkin Medal and received many other honors, but he has one unique distinction; he is the only chemist whose name is indelibly associated with two great processes in two distinct fields. In the petroleum industry the Frasch process means billions of gallons of "skunk oil" sweetened and rendered usable. In the chemical field the Frasch process has produced over 100 million tons of sulfur that, except for it, would have lain buried deep underground, useless.

NOTES AND REFERENCES

There is much first-hand biographical material in the presentation and acceptance addresses at the time of the Perkin Medal award; *Ind. Eng. Chem.*, 4, 138 (1912); *Chem. Met. Eng.*, 10, 78 (1912).

Also, material can be found in the testimony of witnesses and exhibits in the patent infringement suits, *Union Sulphur Co. vs. Freeport Sulphur Co.*, U.S. Dist. Court, Delaware, In Equity No. 336, 1915; U.S. Court of Appeals, 3rd Circuit, Nos. 2391 & 2392, Oct. Term, 1918.

For Frasch's work in petroleum: Allan Nevins, "Study in Power," 2 vols., Scribners, New York, 1953.

Ralph H. and Muriel E. Hidy, "Pioneering in Big Business; 1882-1911," Harper, New York, 1955.

For his work in sulfur, see: W. W. Duecker, *Ind. Eng. Chem.*, 42, 2186 (1950); A. E. Marshall, *Chem. Eng.*, 57, 293 (1950); Williams Haynes, "Brimstone—The Stone That Burns," Van Nostrand, New York, 1959, chapters 4, 5, 6, 7.

HERMAN FRASCH

See also M. Mansbach, *J. Am. Pharm. Assoc.*, 7, 163 (1918); *Dict. Am. Biog.*, VI, 602.

Obituaries: *J. Soc. Chem. Ind.*, May 30, 1914; *Chemiker Zeitung*, June 6, 1914; *World's Work*, July 1914; *N.Y. Times*, May 2, 1914.

WILLIAMS HAYNES

.. 65 ..

INTERLUDE IV:

Scientists and Industrialists

INDEX

- IV. 1. Speciale methodusque und probare Schreift. 409
2. Allerhand Schreift. 406
V. 1. Allerhand Experimenten und Labores pro-
mice et iove. 78
2. Theor. und Manual-Praxis de Jove. ibid.

INDEX RERUM MEMORABILUM HUIUS OPERIS.

- A.
Actum verum radicum. 482, 515, 516
Philosophorum commune. 483
sum cataphor. ibid. 514
Præparatio. 499
Accretum. 499
Tetraent. rub. 748
Accretum hominum, animalium, herba-
rum & metallorum quid? 70-31
Agens & Patens ad quibet modum per-
tinet. 115
Universale Philosophorum quid? 99
Agentia externa, quid Philosophi vocant. 94
Albedo, perfectum lignum bonæ operatio-
nis. 57
Alchymia, perfectum est scientia naturalis. 29
qui scientia causæ naturalis. ibid.
pernosa avaria. ibid.
Theoria & Praxis facilis. ibid.
natura simplex. ibid.
cur Juvenes potius ad artem hanc per-
veniant. ibid.
futilis speculatio vinanda. ibid.
sine multiplicatione feminis metallici
est scientia inutilis & damnosa. 48
quomodo rectè practici potest. 79
perit plerumque avari. 89
scientia quomodo acquiritur. 90
Procelsum confilium in tribus punctis
quæstio operationis. 90
inventiones & divinationes. 90
nulli confidat. 92

- Ret nobilis. 376
& Astronomie Concordantia. 476
Alamen Saccharum ex Virola. 517, 544
Animæ alba & nigra und Natur. 14 464 165
171.
Aqua solvendi seu solutiva Minerales
optimæ. 464
Solutivæ live mensuris Philosophici ve-
ta descriptio. 479, 519
fixiva, obet. 519, 520, 521, 522, 523
ad vitiandum. 205, 524
Theophrasti. 219
extracho et a terra. 312
seu. 365
alud cum Talco. 366, 400, 499, 504
774
Dad Patrem cum Parte fight. 701
præparatio. 729
Julius von Hardick. 807
ad vitiandum. 809
reidit ad vitiandum solvendi.
Aqua ad præparandum. 410, 441
Aqua rubra. 355
nostra quid? 41
Aqua viæ Philosophorum & vinum vitæ
Theophrasti. 436
Aque Regi distillatio. 435
Aqua rubicundissima ex S & G. 415
ibid. 470
Aqua Satani præparatio. 392
Aquila

RERUM MEMORABILUM.

- Aquila præcipitata. 508
Archæa mineralis, & quæ ignia Philosopho-
rum vocatur. 116
Qualitates in ordine mixtionis & milic-
bilium cum quinquæ observationibus. 117, 119
notitia & recommendatio. 127
Argentum & Adm. accidentia. 8
Accidit quatuor: 1. incombustibilitas,
2. pendurabilitas in igne, 3. puritas Efflu-
4. densitas & pondus. 8-9
Proprietas. 8
duplici demonstratione investi-
ganda. 8
materia proxima apud Artem & quod
dividuum & individuum. 7
demonstratio prima est confirmata sub-
stantium. 8
demonstratio secunda proprietates & ha-
bitus materia. ibid.
per non inflam mentur nec exurantur.
partes essentielles igne non dissolu-
tur. 9
metalla tenuissima & quare. ibid.
Argentum & aurum causæ efficientis, natura, vi-
sua, qualitas, actiones, opera & motus,
quid? 11, 13, 14 15, 16, ejusdem definitio, vi-
sio & explicatio. 17
luminis investigationis solam incumben-
dum. 22
tria & venter celata. ibid.
luminis & aurum naturalis ut plantarum &
animalium. 21, 26
celsitudo Raymundi Lullii. 219
fubstantia secundum Kelscum Cent. 3.
5. 73. 798
Argentum, mater tinctorum. 31

- Argentum vivum apud artem proxima ma-
teria auro & argento. 10, 17
insimilitudo substantiæ argenti & au-
rum refert. 10
propria & communia accidentia cum
argento & auro habet. 10
pondus eam auro. 11
quid sit. 11, 64, 94
causa efficiens. 17
minus quid? 17, fit concoctione. 18
quomodo & cui causa efficiens con-
coctione perficitur matiam proxi-
mum. 18
Præparatio. 19
vivum animatum metaphoricè quid
sit? & viæ veterum Philosophorum
dicitur. 19, 20
semen femininum in metallis. 3 41, 51.
64, 165
cur pro humido radicali metallorum fla-
tuum. 31
Argentum vivum Proportionem habet erga
Sulphur metallicum. 32
Exemplum finationis. ibid.
analogia cum aqua pluviali & sanguine
mensurali. ibid.
cur pro humido radicali metallorum fla-
tuendum. 32
humor conaturalis homogeneus. 32
habet proportionem erga sulphur me-
talicum. ibid.
citus à forma sulphuris coagulati &
transmutari potest, quom materia ve-
getabilis & animalium. 33
dicitur sulphure puro. ibid.
cur Chymici primam materiam Metal-
lorum vocant. 36
potentia solvendi in Mercurio. 44, 45
k k k k k
Argenti

INDEX

- Argenti vivi mutatio in substantia & qualita-
te, ejusque multæ & multonis propieta-
tes, Alteratio, Accretio & diminutio al-
terationis & multonis. 53, 54, 55
non omne ad Tincturam urit. 64
Aurum Crelescentia & aurea herba. 494
digestio. 574
separatio à g. 576
Seminis Præparatio. 270
Spiritus Ferdinandus III. 260
Ejusdem rectificatio. 262
Gradatio. 407
solutio secretæ, verè Philo- phica. 246
mollit inest terre, quæ damnata seu
morta, seu marita vocatur. 37
Eniores circa Mercurationem. 18
animum extr. hinc magnum arcum. 48
multiplicandi possibilitas physicæ tam
necessaria quam fermenti multipli-
cationis. 49
Extenuatio physica. 71
Extenuatio mechanica. ibid.
Auri recenteratio. ibid.
augmentatio qualitativa movente Ar-
cheo minerali. 118
Cementatio & augmentatio. 751
separatio à Pa. 789
augmentatio à Digboz facta. 796
Aurum non cedit igni, & quare. 37
pater tinctorum. 31
cur mortuum vocatur
vulgare à Philosophis. 65
caelum à Philosophis vocatur. 272
diaphoreticum. 467
Philosophorum quid? 475, 492
Chymia Christiani (fines) Cognis. 507
Quædam Errata. 509
alud. ibid.

- alud ad Metallum sui solvitur. ibid.
alud. 210
alud. 246
Arsi idem operis materiam, quibus natura, &
produci quod perfectus natura. 43
B.
Brumazar, quid est? 19
C.
Calcinatione comparata cum præparatione ce-
restica. 58, 59
nes due apud Philosophos, nempè so-
phistica & philosophica. 67
sophistica quomodo fit
philosophica quomodo fit
est philosophorum solutio
philosophica, quid sit
Lu 23 guini
Soli Beguni
Calci cupulibet corporis solutio
Calci Philosophorum vegetationem retinet. 98
Calor & frigoris causa efficiens corporum simi-
lariū & naturalium. 14, 15
Canis materia proxima semen caninum. 7
Carmina quædam de quodam particulari
ex. 578
Crystalli sublimati
ex g. 273, 469
Præparatio. 472, 499
Chymia nullam p. citur simulationem coram
Deo. 27
beneficium & damnum in dando vel
negando. ibid.
Authoritas. ibid.
Potentia. ibid.
divinitus infinitæ
redius perpetui & honesti
multiplicatio in perpetuum
mali modi acquiritur
maledicta acquiritur
Emptio

RERUM MEMORABILUM.

- Emptio perperitiosus Processus. ibid.
perpetuum studium & labor. ibid.
Chymia scientia quomodo acquiritur, non vi
vel imperii, sed sola vocatione divina
& libri legendis. 18, 89
via erroris. 89
in 3. Classes distributa. 71, 72
requisitæ patientiam
artis compendium. 107
quinque articuli. 1. de Chymici veri in-
tentione. 2. de Chymie magnifi-
centia. 3. de præparata intentione qua-
rentium hanc artem. ibid. 4. de vera
& naturali scientia hujus artis. 5. de
Praxis methodo laborandi
Constitutio secunda principalis operatio in
opere philosophico. 66
quomodo fieri debet. 487, 518
Colorem statui. 70
Concoctio, quid est? 18
Corallinum Arcanum Theophrasti Paracelli
& Joh. Baptiste Helmontii. 763
Corallorum Essentia. 448
Tinctura. 767
Ctocius Præparatio 390, 565, 728, 734, 788
O. G. O. G. conficiendi verus modus. 555
O. G. O. G. operatio ad O. G. O. G. 553
O. G. O. G. in solvendum. 565
Crocus gis, obet. ad gradationem Solis &
D. gis. 549
S. 214
Crollii Arcanum. 215
Cyni philosophici descriptio. 245
Decompositio Principii salini auri, in ordi-
nem ad Tincturam. 125
Principii Sulphurei auri ad eundem fi-
nem. 125
Principii Mercuriali ad Tincturam, ibid.

- Differentiæ viginti duo Philosophicæ. 63
F.
Fermentationes due apud Philosophos nempè
fermentatio per autum phycum
& vulgare. 65
per autum Phycum quomodo fit. 65
vulgare. ibid.
Fermenti & Fermentandi Qualitates Symbo-
licæ. 72
Philosophicum, & absq. illo nihil ope-
rari memento. 489, 539
omnia in liquido conjungenda, si recta
effe debeant. 490, 539
Fragmenta varia de Sale Philosophi. 377, 469
Generatio sine femine nulla fieri potest. 37
I.
Ignis, quæ sunt ignes separat Argentum vi-
vum à corporibus. 17
seu forma Philosophorum non vide-
tur. 41
entrescat necessari. 41
extensus excitat ignem internum, qui est
causa veræ mixtionis. 58
duplex apud Philosophos, nempè com-
munis & Philosophorum. 68
communis. ibid.
Philosophorum. ibid.
Regimen in prima rotatione. ibid.
in secunda. ibid.
L.
Laborandi Praxis, Method. & causa. 74, 569
Lac Virginis schidii maqum. 459, 224
Lapidis natura triplex. 21
vegetabilis. ibid.
animalitas. ibid.
mineralitas. ibid.
nomen, natura & virtus. 23
Lapidis Philosophorum materia quid? 493
Obabit

The first 4 pages of the Latin index, a real table of contents, alphabetically arranged, from Johann Joachim Becher's *Chymischer glücks-hafen oder Grosse Chymische Concordanz und Collection*, Frankfurt, Johann Georg Schiele, 1682.

CHEMISTS can be grouped together in several different ways according to which traits are considered important. A particularly appealing method for doing this consists in forming pairs of opposites characterized by being more or less completely exclusive. However, just as in setting up types of personalities, many transitions will be found, and their importance will grow with continued study.

This will certainly also apply to the attempted grouping in this chapter of chemists into scientists and industrialists. The two groups do not really exclude each other, because they tend either to make science more industrially minded or industry more scientific.

The discussion of chemists in their relationship to science and industry will provide the occasion to mention some of those many great men to whom separate biographies have not been devoted in this book.

In early times chemistry was not a full-time occupation. The anonymous ancient brewers, tanners, metal workers, and makers of glass and pottery knew everything about what they were to do; tradition told them so. Philosophers, physicians, and pharmacists discovered questions of chemical nature, thought and wrote about them. They became chemists for part of their working time. A few experiments were sufficient to give decisive answers to new questions, because well-established authority was available to explain them. Robert Boyle's skepticism (p. 136) sounded a warning without immediate resonance. His strength as a chemical scientist was still based on philosophy.

A rare combination of philosophy with interest in business enterprises and chemical experimentation dominated the variegated life of Johann Joachim Becher (1635–1682), the "Med. Doct. and Röm. Kays. Maj. Cammer- und Commerzien- Rath" from Speyer, as he identified himself on the title page of his 810-page book: "Chymischer glückshafen oder grosse Chymische Concordanz und

Collection." Frankfurt, 1682. Equally famous was his "Chymisches Laboratorium, oder Unter-irdische naturkündigung," Frankfurt, 1690, based on his "Actorum laboratorii chimici monacensis, sed Physicae subterraneae libri duo" of 1669. His biographer, Urban Gottfried Buchern (Nürnberg and Althoff, 1722), saw in him "das Muster eines Nützlich-Gelehrten" (the paragon of a useful scholar). He won lasting fame through Georg Ernst Stahl (1660–1734), professor of medicine in Halle from 1694, who developed Becher's *terra pinguis* into phlogiston, the mysterious substance forming a principle of all combustion.

Rudolph Glauber (p. 116) was among the first to combine science with industry. In the eighteenth century several scientists manifested interest in the developing chemical industry. Jean Hellot (1685–1766) worked and wrote on the dyeing of wool and woolen fabrics (1750) and collaborated with Duhamel du Monceau (p. 178) toward the improvement of mining operations. Jean Antoine Claude Chaptal (1756–1832), a physician, became professor of chemistry at Montpellier where he had established the first commercial production of sulfuric acid in France. Louis XVI created him Comte de Chanteloup, and Napoleon bestowed many honors on him. From 1819 to his death Chaptal was active in the Chamber of Peers and in many public commissions. All the political upheavals did not change the fact that he was needed as a chemist, economist, and administrator. His two volumes on the use of chemistry in agriculture appeared in 1823, ten years after Davy's effort in this direction, and seventeen years before Liebig's exciting book.

Many of the great chemists in France were appointed by the government to administrative positions in industry, like Claude Louis Berthollet (p. 316). Gay-Lussac (p. 360) did much for chemical engineering, particularly in improving the manufacture of sulfuric acid. Leopold Gmelin (p. 454), so widely associated with the new rise of inorganic chemical science, ventured into industrial pursuits. James Muspratt (1793–1886) who had learned his chemistry mainly from books, like Nicholson's Dictionary (1808), started the manufacture of soda by the Leblanc process in 1822 near Liverpool and saw his son Sheridan publish a book

in 1860 on "Chemistry, Theoretical, Practical, and Analytical, as applied and relating to the Arts and Manufactures" which gave to many young chemists the guidance that James had obtained from Nicholson's old book.

Friedlieb Ferdinand Runge (1794–1867) began his chemical career as an apothecary's apprentice in Lübeck in 1810. He received his M.D. in Jena in 1819, and his Ph.D. in Berlin in 1822. In 1816 he discovered that an extract from belladonna enlarged the pupil of the eye. Three years later he obtained, as a present, some coffee beans from Goethe and extracted caffeine from them. He could have devoted all his further work to the study of the alkaloids, but his affiliation with a textile plant in 1826 and a chemical manufacturing plant from 1831 to the end of his life developed other interests. Investigating the products from coal tar distillation, he discovered aniline, pyrrole, phenol, and rosolic acid. He tried his hand in making soaps, candles, sugar, and ink.

A textbook on the chemistry of dyes and dyeing appeared in three volumes which he published separately in 1834, 1842, and 1850. In the third of these volumes, he described the capillary action of blotting paper and demonstrated its use for determining the end point in precipitating dyes from their solutions. This can be considered the beginning of paper chromatography. He continued such studies on dyestuffs and published two collections of patterns, the second in 1855 under the philosophical title: "*Der Bildungstrieb der Stoffe*" (the formative tendency of the substances).

Runge resembles Scheele in some respects; both discovered many new substances and sought the general theory linking some of their special experimental results. They differ in Runge's greater preoccupation with industrial chemistry.

When a science grows, it creates its own impetus to further development. Creative men learn from their predecessors how to surpass them in extending the field of knowledge. Toward the end of the eighteenth century, chemistry had grown considerably in size. Peter Joseph Macquer's dictionary of chemistry comprised seven stout volumes (almost 6000 pages) in its second edition by Johann Gottfried Leonhardi, 1788–1791. Yet, even the great La-

voisier (p. 264) spent only a small part of his time in chemical research; for the rest of the time he was an economist, agriculturist, and businessman.

Berzelius (p. 386) was probably the first full-time chemist. Although for the most part he worked alone in his laboratory, he kept in personal contact with the young chemists of Europe and exerted great influence through his writings more than by his teaching. This influence had not penetrated to the popular level when young Liebig (p. 536) declared he wanted to study chemistry and encountered derisive laughter. He showed that chemistry is a worthwhile science to follow and that it had profitable applications. He demonstrated this when he explained to a manufacturer of Prussian blue that it was not the noise of his mixing equipment that assured a good product, but the addition of some iron to the mixture, an addition better made separately than by abrading the walls of his vessels. He ended it by demonstrating and pleading the use of chemistry in agriculture and nutrition. Although he did not become an industrialist, he went from pure chemistry to its applications.

At an early age, Charles-Frédéric Kuhlmann (1803–1881) began to combine science with industry. Later on, he also took an active part in community affairs, not in his native town of Colmar, Alsace, but in Lille in northern France, near the Belgian border. He began his chemical training with Louis Nicholas Vauquelin (1763–1829), a great experimenter who had started in very modest circumstances under Antoine François de Fourcroy (1755–1809), like Faraday under Humphry Davy, and who discovered the elements chromium and beryllium.

In 1823, Kuhlmann founded and financed a chair of chemistry applied to the arts and industry in Lille. Two years later, he started to manufacture sulfuric acid with two lead chambers. Soon he added a plant to make soda by the process of the unfortunate physician and inventor Nicolas Leblanc (1742–1806). This process started with the conversion of salt into "saltcake," sodium sulfate, which was then calcined with charcoal and ground limestone. The hydrochloric acid liberated in this first step was usually sent through the smokestack to contaminate the air. Kuhlmann,

however, utilized it to digest bones and thus improve their fertilizing value, particularly for sugar beets. In another connection with the new beet sugar industry, Kuhlmann regenerated the bone black, used for decolorizing the sugar solutions, by treating it with his soda by-product, hydrochloric acid.

In December, 1838, he reported before the Scientific Society of Lille on his experiments on nitric acid from ammonia. His method made use of "the little known force that had been called catalysis by Berzelius" (just a few years before). He passed a mixture of air and ammonia gas through a glass tube partially filled with the finely divided platinum called platinum sponge. Nothing happened at room temperature, but when the tube was heated to 300° , the platinum started to glow red, and the outgoing gas contained vapors of nitric and nitrous acids. He recommended this reaction, and the use of platinum sponge in general, to the attention of chemical manufacturers, because, as he said in 1847, here was a possibility of making France independent from importing the nitrates and nitric acid that are so important in wartime!

Upon the creation of a *Faculté des Sciences* at Lille in 1854, he retired from his teaching to devote more time to his expanding industrial activities. He bought up two smaller plants, and he added the manufacture of ammonium sulfate from gasworks liquor in 1860. The total of heavy chemicals from his plants reached 60,000 tons a year in 1873. In addition, he was finance director of his adopted town, and he became a member of the legislative body of northern France.

Although a professor, Robert Bunsen (p. 574) was an "applied" chemist almost all the time. In 1838, when he was only twenty-seven years old, he showed how blast furnace operation could be greatly improved by utilizing the wasted gases.

William Henry Perkin (p. 758) represents the rare, and the first, example of a scientist becoming an industrialist and returning to pure science. Otto N. Witt followed this example to a certain extent. Both of these scientists achieved industrial and financial success in the field of synthetic dyestuffs with their inventions. Peter Griess (1829–1888) made fundamental contributions to this field, but others reaped the rewards. As an assistant to A. W. Hof-

mann (p. 626) in London, Griess discovered, in 1858, that highly reactive diazo compounds are formed by treating aniline and other aromatic amines with nitrous acid. After he became a chemist at the large brewery of Alsopp and Sons, he continued his solitary work on diazo compounds and discovered that dyestuffs made from diazotized benzidine can be used for the direct dyeing of cotton. This discovery was of tremendous industrial importance, but his patent application of January 9, 1884, came too late. Paul Böttiger's German patent on these dyestuffs, called Congo red, was issued on February 2, 1884. Heinrich Caro (1834–1910), himself a highly successful industrial dyestuff chemist, said of Peter Griess: "Others have reaped where he had ploughed. Griess was not a lucky inventor."

Baeyer (p. 734), Emil Fischer (p. 982), Tiffeneau (p. 1390) and Richard Willstätter (p. 1366) remained scientists while furnishing chemical industry with new products. In the early part of this century, chemistry was still the exclusive domain of the university professors. Yet what they did often led to new industrial developments. The time it took for theory to become practice was very short in some instances, very long in others. Paul Ehrlich's theoretical work on new therapeutic chemicals was rapidly translated into commercial productions. What Moissan discovered about fluorine, or Alfred Stock and Arthur I. Schlesinger about boron hydrides had to wait for many decades before industry needed and developed them.

Among these great chemists, there were those who pursued science because they needed it as industrialists, like Ernest Solvay (p. 774), and those who applied their scientific knowledge in industry as consultants, like Teeple (p. 1410) and Arthur D. Little (p. 1192). There were also some whose excursions from science into industry were not always successful, like Wilhelm Ostwald (p. 1020). Few scientists were as fortunate as Carl Auer von Welsbach (1858–1929) who translated his own scientific study of the rare earths and platinum metals into their industrial use, particularly of thorium for incandescent gas mantles, osmium for electric lamps, and cerium in alloys with iron. The example of Bunsen, his teacher, inspired him: the Bunsen burner and spectroscopic analysis were among his tools.

Willard H. Dow (p. 1220) became an industrialist by building up an organization of his own. Usually, it was—and remains—rare to find a chemist in top administrative industrial position in this country. It was different in England, France, and Germany. Ludwig Mond (1839–1909) came from Germany and developed a large chemical enterprise in England, the Brunner, Mond et Co. In Germany, Carl Leverkus (1845–1925), Heinrich von Brunck (1847–1911), and Carl Duisberg (1861–1935) acquired prominence as industrialists comparable to that of Carl Bosch (p. 1398).

The scientific schools prepared chemists not only for science, but also for industry. The fact that schools in Germany, after the model set by Liebig, did so more than those in France and England was, in great part, the cause for the exceptional position that German chemical industry acquired in the second half of the nineteenth century and held for decades.

The picture of the chemist as a laboratory worker is quite incomplete. The experiments have to be planned, their results must be calculated and interpreted. Georg Lunge (1839–1923) and Vincent Sidgwick (p. 1376) spent more time at the desk than in the laboratory or the lecture room; the former compiling analytical procedures and describing industrial operations, the latter coordinating and interpreting results of inorganic theoretical chemistry.

Many of the great chemists were great administrators, too, and some of them went far beyond the range of their particular university institutions. Marcelin Berthelot (p. 676) held high offices in the French government. Emanuele Paternò, born December 12, 1847, in Palermo, a student of Cannizzaro's, was very active in political affairs besides being a professor of chemistry at the Universities of Palermo (from 1872) and Rome (1892–1923). He became a senator in 1890, and in 1911 the title Marchese di Sessa was conferred upon him. He died on January 18, 1935.

Nicola Parravano, born July 12, 1883, began his chemical studies under Cannizzaro and obtained his doctor's degree in 1904 under Paternò in Rome. After directing applied chemistry at Padua (from 1913) and physical chemistry at Florence (1915–19) he came to Rome and directed the Institute of Chemistry from 1923 on as Paternò's successor. While doing outstanding work in metallurgy, catalysis, fuels, agricultural chemistry, and radioactivity, he

showed great talent in the administration of science and its applications on a national scale. From 1929, he was head of the Accademia, a prominent and respected figure at all international conferences on chemistry and chemical economics.

Avicenna and Paracelsus, van Helmont and Boerhaave figure as prominently in histories of philosophy and of medicine as in the present volume on chemists. Hermann von Helmholtz (1821–1894), Einstein, and Heisenberg are among the few great scientists of more recent times to whom philosophers pay almost as much attention as do physicists. Modern chemists are absent from this honor roll.

The far-reaching thoughts they developed laid the foundations of chemical industry. Will the time come when chemists are not only scientists and industrialists but also philosophers? It could be only in a reversal of the situation that Robert Boyle so valiantly overcame!

NOTES AND REFERENCES

- 1 About Hellot, see "Mémoires de Paris," 1766, 167 (Paris 1769).
- 2 E. W. D. Tennant, "The Early History of the St. Rollox Chemical Works," *Chem. & Ind. (London)*, 66, 666 (1947).
- 3 J. Pigeire, "La Vie et l'Oeuvre de Chaptal," Spes, Paris, 1932.
- 4 K. R. Webb, J. A. C. Chaptal, *Chem. & Ind. (London)*, 1443 (1956). See also: E. Armstrong and H. S. Lukens, *J. Chem. Educ.*, 13, 257 (1936).
- 5 L. J. M. Coleby, "The Chemical Studies of Macquer," Allen & Umvin, London, 1938.
- 6 M. James, "Alfred du Pont," Bobbs Merrill, New York, 1941.
- 7 H. S. van Kloosters, "Bunsen, Berthelot and Perkin," in *J. Chem. Educ.*, 28, 359 (1951).
- 8 A. W. von Hofmann, Emil Fischer, Heinrich Caro, "Peter Griess," in *Ber. Deut. Chem. Ges.*, 24, R, 1007 and I-XXXVII (1891).
- 9 J. M. Cohen, "The Life of Ludwig Mond," Methuen & Co., London, 1956.
- 10 H. E. Armstrong, "The Mond's and Chemical Industry—a Study in Heredity," *Nature*, 127, 238 (1931).
- 11 H. E. Armstrong, "The Chemical Industry and C. Duisberg," *Nature*, 135, 1021 (1933).
- 12 C. Glaser, Obituary of H. von Brunck, in *Ber. Deut. Chem. Ges.*, 46 I, 353 (1913).

SCIENTISTS AND INDUSTRIALISTS

- 13 J. D'Ans, "Carl Auer von Welsbach," in *Ber. Deut. Chem. Ges.*, 64 A, 49 (1931).
- 14 E. Berl, "Georg Lunge," in *J. Chem. Educ.* 16, 453 (1939).
- 15 W. H. Cliffe, "Peter Griess," *Chem. & Ind.*, 1958, 616.

EDUARD FARBER

.. 66 ..

Jacobus Henricus van't Hoff

1852-1911



JACOBUS HENRICUS VAN'T HOFF was born on August 8, 1852. His father, a physician, was a devoted student of Shakespeare's works. Both the mother and the children were deeply influenced by the father's predilection; often they all sat around the table, each with a copy in hand, following the father as he read aloud from his favorite author.

Young Henry had an appreciative eye for the beauties of nature and was able to describe eloquently what he had seen on his wanderings. At fifteen, he left the elementary school and entered the fourth class of the five-year *Hoogere Burgerschool* in Rotterdam. He became a leader of his class. The chemical instruction inspired him to experiment at home. Having passed the final examinations in 1869, he told his parents that he wished to continue in chemistry. The reaction was similar to that which Liebig experienced at the gymnasium in Darmstadt when his declaration, that he wished to become a chemist, produced scornful laughter. At that time, chemistry was not considered a possible career for normal people. Although conditions in Holland at the time differed from those during Liebig's boyhood, nevertheless van't Hoff's parents could hardly be blamed for objecting to his wish. The outlook for a chemist who planned to devote himself to pure science was far from favorable. Finally, it was agreed that he would study technology at Delft and then go on to the university. He applied himself so earnestly that after two years, instead of the usual three, he received the eagerly desired diploma and was top man in the examination.

The years in Delft were the beginning of a storm-and-stress period in the life of the nineteen-year-old, a period of unrest whose influence can be traced even into the last years of his life. Whereas his friends joyfully indulged in the pleasurable sides of student life, he immersed himself in August Comte's "Cours de philosophie positive." That the young student whole-heartedly accepted Comte as his guide is apparent to all who are acquainted with the elegant, stylized expositions of the French mathematician and philosopher.

Almost every page of his "Cours" contains guiding principles in which it is easy to discover a portion of van't Hoff's work program. Read, for example, the pages in which the French thinker describes the relations between chemistry and physics, or those in which he sketches the road to a more rational investigation in chemistry. "If the immediate relations of chemistry with the science of mathematics, and even with astronomy, are necessarily not extensive from the point of view of doctrine, it is not nearly so with respect to method. In this new sense, it is easy to see, on the contrary, that a sufficient preliminary use, among chemists, of the mathematical spirit and of the astronomical philosophy would inevitably exercise the greatest and most salutary influence on the manner of conceiving and cultivating chemistry, and hence would greatly hasten its later perfection." There is no doubt that these prophetic words contributed in considerable measure to van't Hoff's zeal for self-study of mathematics. With an iron determination, he began at Delft to study calculus; that he set high standards for himself in this regard is clear from his later statement: "My mathematical needs took me to the University of Leiden."

Whewell's "History of the inductive sciences from the earliest to the present time" was also diligently studied, so that the young technical student was now in a position to form an opinion of what the exact sciences had already accomplished and also, perhaps far more important to him, to appreciate the multiplicity of problems that were still unsolved. To obtain an insight into the ways and means by which a knowledge of natural phenomena is acquired and to learn something of the analysis of observational methods, he studied Taine's "De l'intelligence" which could be regarded as a positive psychology. The study of Comte and Whewell soon gave rise to the desire to become acquainted with the stories of the lives of the eminent ancients and moderns with whose mental products he had just become familiar; accordingly he read a number of biographies, acquiring information that stood him in good stead in later years.

However, all this was put definitely in the shade when he began to read Lord Byron's poetic works. In a very short time, he was utterly captivated by the English bard. From then on, the latter was his constant companion, in fact his model, almost his idol—

a fascination that was mirrored throughout van't Hoff's lifetime.

His qualifying examination was passed with flying colors in June, 1872. His decision to devote himself to chemistry remained firm, but he did not wish to continue at Leiden because no facilities or inducements in this direction were available at that university. Moreover, he did not find the atmosphere of the city itself to his liking. In the diary, which he kept in his last years, he noted: "In Leiden all was prose, the surroundings, the city, the people. In Bonn all poetry." Meanwhile the work in the laboratory went on zealously. "I have an excellent place in the laboratory; twelve of us are working in organic chemistry, and I am one of those looking for something new. So every day could be my happiest. Consequently I work very hard, sometimes without pause from 9 in the morning to 6 in the evening." This was written in Bonn, where he had gone, possibly attracted by the beautiful surroundings of the city, possibly by the desire to be under the direct influence of Kekulé. Whether the latter had any effect on him has been doubted by some in view of van't Hoff's statement in later years that Kekulé paid little attention to him. However, it is now generally conceded that Kekulé's work had a far-reaching influence on van't Hoff's development. Kekulé advised him to continue his studies at a large university. His next move was to Paris, where he wished to work for a time under the direction of Wurtz. In the meantime he passed (December 22, 1873) the *Doctoraal Examen* at Utrecht, which qualified him to obtain the doctorate later.

He arrived in Paris early in 1874, but he did not embark on a major piece of work during his stay in the French university. Instead, he enjoyed all the more the discussions which Wurtz held in the laboratory with the older students. Among them, van't Hoff was attracted especially by one whose name was destined to be linked with his own, namely, Joseph Achille Le Bel (1847-1930), an Alsatian. At this time, the same thoughts were going through the minds of both, but neither mentioned his ideas to the other.

Van't Hoff did not stay long in Paris. His parents were impatiently awaiting the day when he would complete his university studies by acquiring the doctorate. So he returned to Holland bearing excellent testimonials from Kekulé and Wurtz. But before starting on his doctoral work, the candidate, now only twenty-two,

astounded the Dutch scientific world in September, 1874, with an 11-page paper in his native language bearing the lengthy title: "Proposal for the extension of the formulas now in use in chemistry into space, together with a related remark on the relation between the optical rotating power and the chemical constitution of organic compounds." There is no mention of the name of the author on the title page; it is found only at the close of the paper. Several months later, at the suggestion of Buys Ballot, professor of physics at Utrecht, a French translation appeared with the title: "Sur les formules de structure dans l'Espace" van't Hoff was disappointed in his hope, expressed in the paper, that his views would stimulate a discussion in chemical circles. The time was simply not ripe for this step forward. On December 22, 1874, van't Hoff was awarded the degree *Matheseos Magister et philosophiae naturalis Doctor* at Utrecht, after he had defended his unimportant dissertation "Contribution to the knowledge of cyanoacetic acid and malonic acid" along with 32 theses. Even though one of the distinguished examiners told the young doctor: "Holland has a great shortage of men like you," this was rather a tribute to his general talent than to the merit of the dissertation. Returning home, he busied himself with the preparation of a French version of his Dutch article on the arrangement of atoms in space, which was published in 1875 with the title "La chimie dans l'Espace." He also began to seek a position, but without success. Finally, he was appointed assistant teacher in the Veterinary School at Utrecht, where he taught physics.

An incident occurred in November, 1875, which was important with respect to the rapid dissemination of the theory of the asymmetric carbon atom in that it brought this theory to the attention to the chemical world. Johannes Wislicenus,¹ who was then professor at Würzburg, inquired of van't Hoff whether he would give permission for a translation of his "Chimie dans l'Espace" by Dr. Herrmann, an assistant at Würzburg. In the letter Wislicenus said: "May I inform you that your theoretical development has given me much pleasure and great enjoyment, and in it I see not only an unusually ingenious attempt to explain facts that hitherto have not been cleared up, but I also believe that it will provide a goodly number of suggestions for our science and hence will be of

epoch-making significance." The translation by Herrmann was published in 1876 under the title "Die Lagerung der Atome in Raume" with a foreword by Wislicenus. Like Byron after the appearance of his "Childe Harold," van't Hoff could now say, "I awoke one morning and found myself famous."

The brilliant development of the van't Hoff-Le Bel theory, i.e., stereochemistry, has certainly proved the error of the bitter criticism it originally engendered, especially from the pen of Kolbe.²

Even though some chemists feel that the theory of the asymmetric carbon has merely an historical and didactic significance, that as a theory it has had its day, nevertheless a look at the development of organic chemistry since 1874 reveals what an extraordinary, fruitful effect it has had on chemistry and its applications.

Only a few months after Kolbe's scathing criticism appeared, van't Hoff was appointed lecturer at the University of Amsterdam, where he later served as head of the department of chemistry from 1878 to 1896. His appointment was doubtless due to J. W. Gunning (1827-1900), professor of chemistry and pharmacy at Amsterdam from 1865. He became a lifelong friend to van't Hoff.

In reviewing the development of van't Hoff, it is not difficult to discern the roots of his "Views on organic chemistry" (1878, 1883) in the doctrines of Auguste Comte. The latter, in his "Philosophie positive," expresses the hope, in the pages devoted to chemistry, that he will succeed "in making some of the eminent minds which cultivate this fine science today realize the necessity of submitting all of the fundamental conceptions which compose it to a new and more rational elaboration." This path was followed by van't Hoff in his text, concerning which he himself stated in 1894, on the occasion of his lecture "How the theory of solutions arose": "Young as I was, I wished at that time to learn the relations between constitution and *chemical* properties. After all, the constitutional formula should eventually be the expression of the whole chemical behavior. . . . Thus there came into being my 'Views on organic chemistry,' which you surely do not know. Moreover, it is hardly worth while. However, to me it had the value that it sharply revealed to me an existing gap." The closing of this gap, and much that was of more importance, was accomplished by his "Études de dynamique chimique" (1884). This

book dealt not only with reaction rates, as indicated by the title, but in addition he discussed there the theory of equilibrium and the theory of affinity in such detail and extent that it seems justifiable to speak of a new *revolution chimique* taking place at that time, a turn in the course of chemical thinking whose consequences can be seen even up to the present in purely scientific fields as well as in the technical applications of science. The principal topics, such as principle of mobile equilibrium, condensed systems, transition temperature, measurement of electro-affinity, etc., attest to the service which this important book wrought. Admittedly, it met the same indifference initially that greeted his first book on the arrangement of atoms in space, but a review by Arrhenius in the *Nordisk Revy* (Uppsala) changed this situation. The review closes: "It has been the intention of the reviewer to call attention to the vast perspectives which the work of the author has opened for future research."

Since in none of his other books did van't Hoff appear so notably as an experimenter as in the "Études," it is well to point out this feature since there is a widespread opinion that his importance as a laboratory worker was of little weight. During his student career, he was anything but a deft manipulator, but thanks to his innate persistence and diligence, he knew how to acquire what was necessary in a short time. Convinced of the correctness of the dictum: "It is not sufficient to know the principles, it is necessary to know how to manipulate," it must have weighed on his mind that he could not afford to be lacking in a talent which he considered of prime importance for attaining success in his chosen science. Consequently, in Utrecht and later in Amsterdam he made every effort to develop new though simple equipment in order to acquire the requisite experimental skill. The difficult experiments in fields first cultivated by him such as the ones included in the "Études" give ample opportunity to see how far he approached this goal by self-training. Whoever saw him at work could testify that he arrived at an elegance in manipulation that could be the envy of many an experimenter. His chief aim was always to reach the desired goal with the simplest equipment in order to avoid as much as possible the less accurate corrections to which he had a pronounced antipathy. A typical instance is afforded by the

great mass of important facts which he and his students gathered by means of the rather simple "dilatometer."

The ideas which van't Hoff developed in his papers submitted to the Swedish Academy of Sciences (1885), namely, "The laws of chemical equilibrium in the dilute, gaseous or dissolved state," "A general property of dilute matter," and "Electrical conditions of chemical equilibrium" have now become common property. However, at the time, the seed fell on fertile soil only in a single instance, and even this became apparent only after some time. It was Svante Arrhenius who appreciated the great significance of the van't Hoff theory of dilute solutions along with their relation to his own studies of electrolytic dissociation in dilute solutions. Accordingly, Arrhenius soon arrived in Amsterdam to remove the existing difficulties through intensive investigations. It is now generally known how this collaboration led to a theory of dilute solutions in the broader sense, and most chemists are aware of the great opposition that had to be overcome before this theory was accepted, an advance due in large measure to the efforts of Wilhelm Ostwald, the propagator of the new school of thought. No less important in the rapid development and dissemination of the new ideas was the *Zeitschrift für physikalische Chemie, Stoichiometrie und Verwandtschaftslehre*, founded in 1887 by Ostwald and van't Hoff. These ideas were fruitful in other sciences, particularly physiology. However, it must be recognized that the much too sanguine hopes of many physiologists were not fulfilled, and Pekelharing was correct when, in 1904, he presented van't Hoff with an honorary doctorate of medicine at Utrecht on the occasion of the dedication there of the van't Hoff Laboratory and said: "Whoever attempts with insufficient knowledge to apply physical chemistry to the processes occurring in the living organism, runs the risk—as has already been amply shown by experience—of coming to false conclusions."

Numerous young men soon came to Amsterdam from many countries to pursue their studies under van't Hoff's guidance. He was soon the recipient of many distinctions, including the Davy Medal of the Royal Society in London and the first Nobel Prize in chemistry (1901). In 1887 he received a call from the University of Leipzig. This catalyzed the Amsterdam authorities into

providing the funds for a new laboratory, which was put into service in 1892. In the meanwhile the work had piled up so much that he sought means for obtaining relief from those duties which could be satisfactorily turned over to younger men, such as the lectures to medical students.

His intensive mental labors, the uninterrupted bodily strain required by the experimental researches, the wearing administrative tasks of the laboratory had a deep-seated effect on van't Hoff, an effect which was revealed plainly in later years when conditions had altered. There is little doubt that in Amsterdam he was a very different person than in Berlin, where he moved in 1896. Although a new laboratory had been built for him at Amsterdam, there was no lightening of his work load. His excellent health, his creative ability, which never sagged even when most taxing studies were under way, made it possible for him to meet the high demands he imposed on himself. A difficult task once completed, his mental abilities were readily restored by a period of rest and recreation. But eventually, the excessive demands which the Amsterdam post constantly made of him wore down his resistance; after long and careful consideration he accepted the distinguished invitation of the Prussian Academy of Sciences to make his home in Berlin. His time would now be his own, he could devote himself completely to his scientific work, and if he chose he could continue his pedagogic role by a weekly lecture at the University.

This move resulted in his "Vorlesungen über theoretische und physikalische Chemie" (1898), which was translated into many languages, and also his "Chemische Grundlehren nach Menge, Mass und Zeit" (1912). Furthermore, he now had the time to lecture to wider circles in Europe and America on the results of his work, satisfying a desire that he had nourished in vain for many years. But this was all incidental in comparison to the research projects which he conducted in his new surroundings with the assistance of collaborators from many countries and which he brought to a considerable degree of conclusion. The topic with which he and his co-workers were engaged was an intensive study of the conditions of the formation of oceanic salt deposits, particularly those being worked at Stassfurt. The question he wished to solve was divided into a number of parts: (1) What materials

result if the individual salts, from which the Stassfurt minerals are constructed, are placed in water in any chosen quantities and the mixture is evaporated at constant temperature? (2) In what form, in what order, and in what amounts do these materials make their appearance? (3) What roles are played in this process by time, temperature, and pressure? Heinrich Precht (1853–1924), an acknowledged authority on the German potash industry, stated: "The studies conducted in Germany by van't Hoff benefited the potash industry especially. Many may regard them as theoretical investigations, but whoever has studied them in detail will appreciate the advantage they brought to the industry. Through his lectures in many countries, van't Hoff awakened interest in the potash industry to such an extent that it is impossible to evaluate the material value of these researches." van't Hoff brilliantly attained the goal he had initially set for himself when he moved to his new home, namely, to undertake a study of distinct German national flavor. If perhaps there are some who believe that a man of lesser stature could have carried such a task of self-denial to completion, it is enough to remind such carping critics that: "We should be thankful for a man such as he, who for the public good does something which is not glamorous."

A perusal of the diary which van't Hoff started in 1903 and continued almost to his death, will yield not only short statements about his commissions and omissions, but an insight into his particular state of mind and innermost thoughts. Thus he reports in these pages on the many cultural activities to which he devoted his hours of leisure, particularly the books he was reading. Many troubled thoughts are set down, because even this great man was not spared great sorrow. There gradually developed the pulmonary tubercular condition to which he finally succumbed. He, like his model Lord Byron, had always had a horror of having to endure pain. He was spared this ordeal, and several times he declared that there was nothing of which he could complain.

He died on March 1, 1911. The body was cremated and the ashes repose in the cemetery at Berlin-Dahlem. A lifelike marble relief portrait may be seen in the van't Hoff laboratory at Utrecht, and a bronze replica has been placed in the laboratory which he built and directed at Amsterdam.

GENERAL REFERENCES

- Ernst Cohen, "Jacobus Henricus van't Hoff, sein Leben und Wirken," Akademische Verlagsgesellschaft, Leipzig, 1912.
- A. F. Holleman, "My Reminiscences of van't Hoff," *J. Chem. Educ.*, 29, 379 (1952).
- H. S. van Klooster, "van't Hoff in Retrospect," *ibid.*, p. 367.

NOTES AND REFERENCES

- 1 Johannes Wislicenus (1835–1902) taught at Zürich and Würzburg and succeeded Kolbe at Leipsic in 1885. He made valuable contributions on stereoisomerism, acetoacetic ester, etc.
- 2 Hermann Kolbe, *J. prakt. Chemie* [2], 15, 474 (1877).

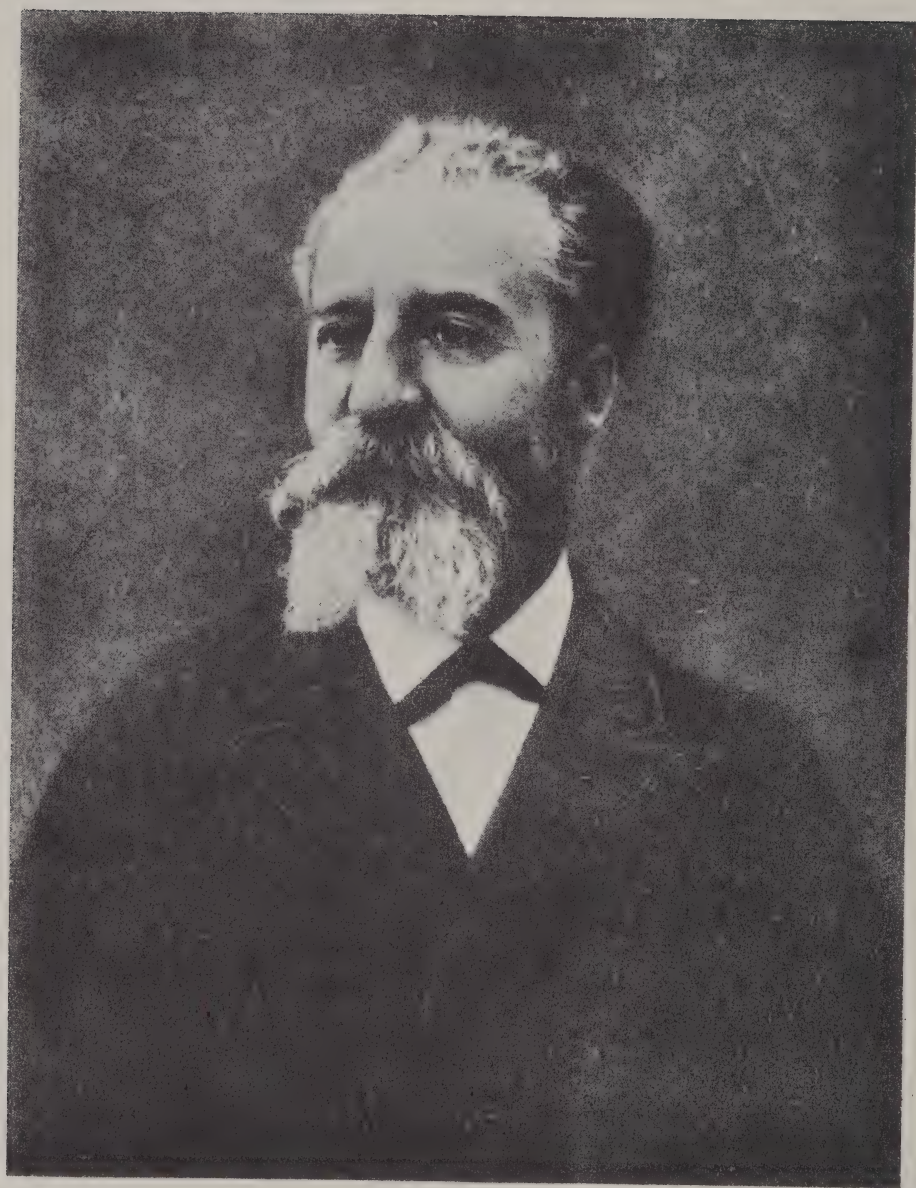
Frhm: Bugge, "Das Buch der Grossen Chemiker," 2, 391–407.
Translated by Ralph E. Oesper.

ERNST COHEN

.. 67 ..

Henri Moissan

1852-1907



FERDINAND FRÉDÉRIC HENRI MOISSAN was born in Paris on September 28, 1852. His father was a minor official in the Compagnie des Chemins de Fer de l'Est; the mother aided the family income by sewing. The family came from Toulouse, a fact reflected in the looks and behavior of Henri Moissan. Throughout his life, his dark twinkling eyes, the unusual mobility of his gestures and his mode of thought betrayed his southern origin. In 1864 the family moved to the little city of Meaux (Seine-et-Marne) where his father, who later was praised for his perspicacity, allowed his son to enter the Collège municipal. There an excellent teacher of mathematics and sciences, James, sensed the outstanding endowment of the boy and encouraged him by free private instruction. Moissan in later years always remembered with sincere appreciation these services by his former teacher who, as he said: "fit naître en lui le goût travaille." Under his guidance, an interest in chemistry was awakened in the young Henri, which held him fast; this preoccupation obviously displeased the other instructors, since when Moissan left the Collège in 1870 he had not attained any kind of university rank.

In order to become self-supporting as soon as possible, but without forsaking completely his beloved chemistry, he became an apprentice in a druggist's shop in Paris. Here his chemical knowledge brought him his first practical success when he saved the life of a person who had been poisoned with arsenic. Despite this feat, he was not satisfied with his position. Conversations with his school friend, Jules Plicque, who was working in a laboratory headed by Dehérain at the Musée d'Histoire naturelle, led Moissan to resolve to devote himself entirely to chemistry. In December, 1872, he began to study chemistry in the laboratory conducted by Fremy in the Musée d'Histoire naturelle. He earned his living expenses by giving private lessons. He planned to enter industry as soon as possible, and set as his goal an annual income of 3600 francs. In 1874, he joined his friend Plicque in Dehérain's laboratory. The latter soon took note of his new student and was

attracted by him. Without trying to dissuade Moissan from his plan to go into industry, Dehérain pointed out that it might be of value to him sometime to secure an academic degree. The advice fell on fertile ground. Although it was difficult for him to cut down on his chemical work, Moissan started to make up his lower school deficiencies and studied first ancient languages and then physics. After several fruitless attempts, he passed the examination for the bachelor's degree in 1874, and in 1877 he became Licencié ès Sciences (B.Sc.).

Moissan's first scientific activity naturally was directed to the field pursued by Dehérain, namely, plant physiological chemistry. As early as 1874, they published in the *Comptes rendus* of the Académie a joint paper; "De l'absorption d'oxygène et de l'émission d'acide carbonique par les feuilles maintenues à l'obscurité." Later Moissan extended this investigation and used the results in a thesis for his apothecary examination. The essential finding was the definite proof that there is no direct connection between the oxygen uptake and the carbonic acid output by plants. Independent of the former, the carbonic acid is released because of the reactions occurring in the plant, even after days of complete exclusion of oxygen.

However, while he was still engaged in this plant physiological research, Moissan took the step which was of primary importance to him and chemistry: he decided to devote himself to inorganic chemistry. The fact that he did this against the advice of Dehérain, who did not wish to lose his gifted student, testifies to the originality and determination of Moissan's spirit. It should be remembered that, at that time, almost all of the eminent French chemists, as well as their colleagues in other countries, had succumbed to the attractions of the vigorously flourishing organic chemistry. Only a few were dealing with inorganic problems since it was generally assumed that this branch of chemistry had already yielded its finest fruits and the later harvest could only be meager. The best of the isolated French inorganic chemists, such as Henri Sainte-Claire Deville, had turned to problems that were more or less physicochemical in nature, a branch which had long been underestimated and which was just beginning to be appreciated. In a speech delivered by the aged J. B. Dumas in 1876 on the occasion

of the death of Charles Sainte-Claire Deville, the brother of the more famous Henri, he complained: "Our country occupies its place largely in organic chemistry, it neglects far too much the chemistry of inorganic compounds. Let us hope that there will soon arise, in the generation which follows us, a young scientist who will take up once more mineral chemistry and will know how to fertilize and revive it."

Moissan's publications numbered around three hundred; with few exceptions they dealt with inorganic-experimental topics.

His first inorganic research was on pyrophoric iron whose preparation had been described about fifty years earlier by Gustav Magnus (1802–1870), also in a first paper. Soon thereafter, Stro-meyer had maintained that this pyrophoric material was not metallic iron at all but rather ferrous oxide. Magnus contradicted this statement vigorously. The re-examination of the question led to the finding, as is so often the case, that both were correct. The reduction of ferric oxide or the heating of ferrous oxalate yielded initially highly pyrophoric ferrous oxide, which on careful further reduction in a stream of hydrogen was converted into pyrophoric iron. Moissan was able to show that when hydrogen acts on Fe_2O_3 at various temperatures, there result in succession the oxides Fe_3O_4 , FeO , and finally elementary iron. As with the latter, the oxides could be made to yield extremely active modifications by avoiding excessive heating, modifications which differed sharply in their behavior toward oxygen and nitric acid as contrasted with the forms that had been known for a long time.

At the suggestion of Sainte-Claire Deville, Moissan submitted his results to Debray, the discoverer of the ordinary ferrous oxide. His appraisal of the work was most favorable, and from then on he showed the greatest interest in the young chemist.

As already stated, Moissan passed his examination as *pharmacien de 1^{re} classe* in 1879, and in this same year he was appointed Maître de Conférences (lecturer) and Chef de Travaux pratiques de Chimie (laboratory instructor) at the École supérieure de Pharmacie, a connection that was to continue during the most part of his scientific career. Besides he was Répétiteur de Physique (assistant teacher) at the Institut agronomique. In 1880, the degree of Docteur ès Sciences physiques was conferred on him by

the University; the dissertation dealt with the iron oxides. The joys of independent research had completely conquered his former intention to go into industry, especially since he now had a regular though modest income. The fees from private lessons had been his principal means of support until then. His financial situation was also improved when his friend Landrin resigned the direction of the laboratory of the Union des Chambres syndicales. The chief function of this laboratory was to make analyses for private customers. These of course had less interest for Moissan, but gave him the opportunity to carry on his own work, which the other posts he held did not afford. Some earlier work on oxides of chromium was now supplemented by papers on chromium derivatives. He did not succeed in isolating the blue perchromic acid, discovered in 1847 by Barreswil, but he was able (1883) to prove that its formula is H_2CrO_5 ; he regarded it as a combination of CrO_3 with H_2O_2 . A year later he described the crystalline H_2CrO_4 , which corresponds to sulfuric acid.

Although these carefully executed studies were greeted enthusiastically by scientists, they did not meet the favor of the customers of the laboratory, whose analyses received a dilatory treatment. The orders fell off perceptibly; in fact the laboratory had to close its doors after a few years. This did not break Moissan's heart, since in the meantime he had become active in other fields.

In 1882 he married Leonie Lugan, the very young daughter of an apothecary in Meaux, in whose house he had been a welcome guest on his many visits to that city during his student days. The ancestors of M. Lugan had also been apothecaries; one of them had been a friend of the famous Vauquelin, the discoverer of chromium who had likewise started his career with pharmaceutical studies. The marriage was a most happy one and was terminated only by Moissan's death. His wife was his best comrade; she helped him as far as she could in his scientific labors and watched over his health, which he often abused by overwork. Their son, Louis (born 1885) was indoctrinated in chemistry at an early age by his father. M. Lugan proved an ideal father-in-law. He provided the new household with an excellent financial foundation

and advised Moissan to devote himself to scientific work without thought of financial return.

As soon as he found himself on an assured basis, Moissan began an exceptionally diligent and successful research activity which ceased only at his death. From among his many investigations, two chapters proved of special importance. These can be designated as "Fluorine" and "Electric Furnace," respectively. The following discussion will treat these main-lines of research in continuous fashion without regard to the order of the publications. Only the outstanding features can be considered here.

The preparation of free fluorine was one of the great problems which the first brilliant period of inorganic chemistry could not solve. Many had worked on this problem before Moissan. The similarity of hydrofluoric acid to hydrochloric acid had been pointed out as early as 1810 by Ampère and Davy, and there was no longer any doubt that the former contained an unknown element which was named fluorine. Davy's extensive efforts to isolate this element were totally negative. The hoped-for decomposition of fluorides by treatment, in gold or platinum vessels, with chlorine or electricity failed completely. Even so there existed a widespread opinion that fluorine must be an extremely reactive material that tenaciously combined with other elements. The years merely brought confirmation of this idea. The Knox brothers and later Louyet, whose careless handling of hydrogen fluoride cost him his life, unsuccessfully tried to bring about a reaction between chlorine and mercury fluoride. Fremy made some progress. His efforts to secure a reaction between chlorine and oxygen on calcium fluoride were unfruitful but, on the other hand, he, like Gore, who in 1870 was the last before Moissan to attempt to isolate fluorine, made it highly likely that free fluorine resulted transiently from the electrolysis of molten calcium, potassium, and silver fluoride; but at the unavoidably high temperature the fluorine disappeared immediately because it at once attacked the containing vessel and the electrode. No progress followed from the attempt to electrolyze anhydrous hydrogen fluoride, which Fremy was the first to prepare by heating KHF_2 , because the anhydrous acid did not permit passage of the current. When moisture was

present, the products were only hydrogen and oxygen containing ozone.

The memory of Fremy's attempts were still alive in his laboratory and Moissan had learned about these experiments during his term of service there. He told himself that the preparation of free fluorine would have to be done at low temperatures and accordingly would most probably be accomplished with volatile nonmetallic compounds. However, very little was then known about such materials. Boron and silicon fluoride, which Moissan studied again in 1904, proved to be such stable combinations that he immediately became convinced that the reaction between fluorine and boron or silicon must be extremely violent. From that time on he used powdered silicon whenever he wished to test any gas for a possible content of free fluorine. Among fluorides of phosphorus, there was known the gaseous pentafluoride discovered in 1875 by Thorpe, and the phosphorus trifluoride described by Dumas as a liquid boiling at 60° . Struck by the lower volatility of trifluoride, Moissan started his research with an investigation of this compound. He soon announced (1884) several methods of preparing pure PF_3 , which was gaseous, as expected. The most convenient procedure was to heat a mixture of lead fluoride and copper phosphide. The description of these experiments demonstrated the features of all of his later publications, namely, completeness and clarity. The methods of preparation, carefully worked out, were described so precisely that they could be repeated without difficulty; the chemical and most important physical properties of newly prepared substances were determined and reported in detail.

Moissan immediately used the new trifluoride in an experiment which had originally been proposed by Davy. The latter was of the opinion that free fluorine would most probably result from the reaction between oxygen and phosphorus fluoride, conducted in fluorspar vessels, because of the great affinity of phosphorus for oxygen. Davy could not carry out the experiment because the method for preparing phosphorus fluoride compounds was not known at that time. Moissan passed electric sparks through a mixture of phosphorus trifluoride and oxygen. The explosive re-

action, however, did not proceed as expected; instead the product was the new gaseous phosphorus oxyfluoride, POF_3 .

Moissan now changed his plan and attempted to bind the phosphorus of the phosphorus fluorides by means of glowing platinum. Since Fremy had already demonstrated the instability of platinum fluoride when heated, there was no danger that the fluorine would also be bound to the platinum. When Moissan passed the trifluoride over red-hot platinum sponge in a platinum tube, platinum phosphide and phosphorus pentafluoride resulted. Under these conditions, the latter probably immediately yielded a slight quantity of free fluorine; the issuing gas reacted with potassium iodide, silicon, mercury, and phosphorus, which was not the case beforehand. However, no free fluorine could be obtained. The experiments were rather costly since the platinum tube became unusable in a few minutes; consequently, Moissan gave up this line of attack. He, too, had now come to the conclusion that the preparation of fluorine at high temperatures was not feasible because of technical difficulties. Nevertheless, the characteristic fluorine reactions he had already obtained had whipped up his eagerness in much the same way as a detective is stirred when at long last he sees his quarry disappearing around a corner. Moissan, like his predecessors, now enlisted the aid of electrolysis and passed a current through arsenic trifluoride, which is a liquid at room temperatures. He rendered it conductive by adding hydrogen fluoride or potassium fluoride. But in a short time the current would no longer pass because arsenic had been deposited on the cathode; at least this was true of the weak electrical forces then available in the laboratory where he was working. Friedel provided better sources of power but Moissan decided that arsenic trifluoride would have to be abandoned chiefly because he had come to realize that this highly toxic compound was affecting his health.

Fremy and Gore had previously tried the electrolysis of hydrofluoric acid itself. Moissan prepared the anhydrous acid by Fremy's method, i.e., by heating potassium hydrogen fluoride in a platinum retort. He subjected this compound to electrolysis in a platinum U-tube cooled to -50° by methyl chloride. New difficulties arose. Much hydrogen was evolved at the cathode, but

the expected fluorine did not appear at the anode. It was found that the stoppers, which served for the insulated introduction of the anode, had been attacked and carbonized. They were replaced by pieces of fluorspar. The goal was now finally reached. On June 26, 1886, there streamed from the anode compartment a gas which immediately set fire to silicon and also exhibited the marvelous reactivity that had been expected of fluorine. With water it produced ozone; it liberated chlorine from potassium chloride.

On June 28 Debray read to the Académie a short communication by Moissan regarding his discovery, a statement which demonstrates that the critical judgment of its author was not dulled by his brilliant success. Moissan gave a brief account of his experiments and then stated: "It is possible in fact to advance various hypotheses as to the nature of the gas released; the most simple would be that it is fluorine, but it might be possible, for instance, that it is a perfluoride of hydrogen or even a mixture of hydrofluoric acid and ozone sufficiently active to account for the very energetic action which this gas exerts on crystalline silicon."

The validity of these findings had to be demonstrated to a committee appointed by the Académie; the members were Berthelot, Debray, and Fremy. Moissan, of course, made the most careful preparations, but when the committee appeared he obtained no fluorine. In fact, he could not secure any passage of the current through the hydrogen fluoride. After Berthelot sought to comfort the dismayed young scientist by citing the perverseness of inanimate material, the three eminent visitors left. The difficulty was cleared up in a few days. The fault lay in the doubly distilled hydrogen fluoride. In his original trials, Moissan had collected the product driven from the potassium acid fluoride directly in the platinum U-tube used for the electrolysis; the entrained potassium fluoride was caught here and provided the mixture with the conductance which the hydrogen fluoride did not have per se. Moissan now added some of the salt to the hydrogen fluoride before starting the electrolysis and from then on the generation of fluorine proceeded regularly. Of course, exceptions arose later on occasions. It almost seemed as though the fluorine wished to avenge itself on the master for having conquered it. This writer remembers that

the fluorine apparatus failed for some reason when it was to be demonstrated to a student audience and could be shown in action only at the next lecture. The same thing happened during a lecture Moissan delivered in London before the Royal Society.

That fluorine really results from the electrolysis of a solution of potassium fluoride in hydrogen fluoride—electrolysis of hydrofluoric acid is actually as much of a misnomer as electrolysis of water—was demonstrated by Moissan by allowing the gas to be absorbed by heated iron, whereby no hydrogen was liberated. He likewise proved that a mixture of hydrogen fluoride and ozone had no special oxidizing powers.

The energetic action of fluorine on chemical substances was paralleled by the effect of its isolation on the scientific world, which at that time had not yet reached the *nil admirari* state of our time. The la Caze prize of 10,000 francs was awarded by the Académie to Moissan, who used the money to reimburse himself for what he had spent out of his own pocket for these experiments. Four months after the isolation of fluorine, Bouis, professor of toxicology at the École de Pharmacie, died and Moissan applied for the post. The Conseil of the École unanimously recommended his appointment, which was approved on December 30, 1886. He thus finally came into possession of a laboratory of his own, and though it was rather primitive and not very large he made it do until 1899. In 1888, he was elected to the Académie de Médecine in the pharmacy section, and in 1891 he succeeded Cahours in the Académie des Sciences. He had been on the list of candidates in 1888 and 1889, as successor to Debray and Chevreul, but had lost out to the older Schützenberger and Gautier. Until 1891, Moissan worked almost exclusively with studies of fluorine and fluorides. His book "Le Fluor et ses Composés" gives a good picture of his comprehensive researches.

As time went on, he considerably improved the method of preparing fluorine. He removed any hydrogen fluoride by passing the gas over sodium fluoride, and later by condensation with liquid air followed by fractional evaporation. The main advance came with the discovery (1899) that copper apparatus could be substituted for the costly platinum equipment. It was now possible to obtain up to 5 liters of fluorine in one hour. The handling of the gas

was greatly facilitated when it was found (1899) that if moisture was carefully excluded glass is no longer attacked by fluorine; in fact the gas can then be stored for some time in glass vessels over mercury, provided it is protected from vibrations and hence from rupturing of the protective layer of mercury fluoride.

Mostly with the aid of free fluorine, Moissan prepared many new fluorine compounds, some of which he investigated thoroughly and described in excellent individual publications. He enriched organic chemistry (1888 and 1890, in part with Meslans) by describing the gaseous methyl fluoride, ethyl fluoride (b.p. -33°) and isobutyl fluoride, which are best prepared from the corresponding chlorine or iodine derivatives and silver or arsenic fluoride. The reaction between carbon and fluorine led to several carbon fluorides (1890) of which the most interesting was tetrafluormethane (b.p. -15°). It was prepared in pure form from fluorine and methane, chloroform, and carbon tetrachloride, or from the latter and silver fluoride.

Great interest was aroused by the gaseous sulfur fluoride SF_6 (prepared in 1900 in collaboration with Lebeau) because of its composition and its chemical properties. It resembled nitrogen in its chemical indifference and was not affected by heating to redness or by molten alkali. Sulfuryl fluoride prepared (with Lebeau, 1901) from sulfur dioxide and fluorine was fairly stable, whereas thionyl fluoride (1900) obtained from thionyl chloride and arsenic fluoride was quite unstable.

Among the metal fluorides he studied the fluorine derivatives of platinum (1889), of the alkaline earths (1890), of silver (1890, 1895), and of di- and trivalent manganese (1900). Noteworthy fluorine nonmetallic compounds of fluorine included the liquid iodine pentafluoride, IF_5 (1902), and nitryl fluoride, NO_2F (with Lebeau, 1905), a very reactive gas, liquefied at -63° , which like fluorine itself combines with silicon even at room temperature.

A pause in the study of fluorine chemistry came in 1891, and this line of study was vigorously resumed only after the preparation of the gas was made easier through the use of copper apparatus. The years 1891 and 1892 were occupied with successful studies of boron. It, too, was among the elements which were not known in the pure state prior to Moissan. Davy had observed the forma-

tion of the brown element when he subjected fused boron trioxide to a powerful electric current. Later, he and also Gay-Lussac and Thenard prepared it from potassium and boron trioxide. Deville and Wöhler improved this method by substituting sodium for potassium. In his first trials Moissan prepared boron by this procedure and from it he obtained, by heating with hydrogen iodide, the hitherto unknown boron triiodide, BI_3 (1891), which he immediately employed for several interesting reactions.

Since his experiments had shown that the boron which he was using was far from pure, Moissan retested the older procedures for preparing the element and came to the astounding discovery that even the most favorable case yielded a product containing only 70 per cent boron. The remainder consisted of boron trioxide, boron nitride, alkali, and iron. However, he succeeded in improving the reaction between boron trioxide and magnesium, which others had used previously, so that the product contained 94–95 per cent of boron; if the reduction was conducted in an atmosphere of hydrogen the purity rose to 99 per cent. No better method has since been found; all of the other suitable reducing metals form borides which cannot be removed from the reaction product.

A paper on the alkaloid, aricin (with Landrin 1890), and a second one on opium smoke (1892) are reminders that Moissan was professor of toxicology even though his chief interests lay in the inorganic field. He found that the poorer the quality of the opium the greater the content of the more harmful materials in its smoke.

While he was still studying boron, Moissan took up another problem of quite *general* interest: the artificial reproduction of the diamond. "The art of producing diamonds was pursued with the same ardor as was alchemy," wrote Berzelius in 1830. This effort, which earlier had taken very remarkable paths, was put on a firmer foundation after Lavoisier in 1773 had demonstrated, by burning diamonds with oxygen, that the gem consisted of pure carbon. But the artificial production of the diamond remained an unsolved problem one hundred years after Lavoisier's experiment. Although many had thought that they had found a satisfactory method, they invariably were proved wrong. In 1880, Hannay claimed to have obtained diamond chips by heating oils to redness

with metallic lithium, but his claims were never confirmed. Not long after, Marsden said that he could prepare small diamond crystals by fusing silver with sugar charcoal. His paper received no attention, but since Moissan subsequently substantiated this claim by actual trials, Marsden deserves the credit for being the first to have prepared regular crystallized carbon. On the other hand, Moissan was the first to approach the subject in a comprehensive and systematic manner.

In the beginning he hoped—and here is the bridge from his fluorine researches to those dealing with the diamond—to arrive at diamonds by decomposing fluorhydrocarbons, since fluorine had been found to be a distinct “mineralizing” element in numerous instances. However, he obtained nothing but amorphous carbon. In his later trials he followed the paths of Nature herself. Whereas the earlier chemists, even Liebig and Wöhler, had supposed that natural diamonds were formed at relatively low temperatures, Daubrée, on the basis of studies of diamond-bearing meteorites and earths, stated in 1890 that diamonds must be formed under conditions of high heat and much pressure. The uniform development of the diamond crystal in all directions indicated that they are formed in a liquid or at least pliable environment. The fact that many diamonds are optically anisotropic and also that some specimens shatter for no apparent external reason indicates that they have been subjected to high pressure. Moissan himself investigated diamond-bearing earths from Brazil and South Africa. In them he found not only many microscopic diamonds but also graphite, a finding which made the high formation temperature still more likely. Without exception, the diamonds left some ash that contained iron. From this Moissan concluded that they had been formed in an iron-bearing environment and that perhaps, since iron is known to dissolve carbon, that they had simply crystallized out of iron. However, when he tried to prepare diamonds in this manner, he obtained graphite and amorphous carbon exclusively. At first he used an oxygen blast to melt the iron. Since he required higher temperatures than this afforded, he switched to the use of the electric furnace. This apparatus will be discussed later.

Moissan's attempts to prepare diamonds artificially had reached

an impasse when by chance they received a new impulse. On December 12, 1892, Charles Friedel reported to the Académie that he had found many tiny diamonds in a meteorite from Arizona. Moissan himself investigated a piece of this meteoritic iron and in addition to diamonds found that it also contained graphite and amorphous carbon. Previously, he, like many others, had doubted the occurrence of diamonds in meteorites, but now he was convinced that diamonds could arise from carboniferous iron and that he had not employed the proper experimental conditions in his early attempts. He had the happy thought of suddenly cooling molten iron that had been saturated with carbon in the electric furnace. The graphite crucible containing the iron was plunged into water. Carboniferous iron, like water, expands when it solidifies. When rapidly cooled, the outer layer of the metal solidifies first; therefore high pressures were exerted on the interior while the remaining iron became solid. Under these conditions, a portion of the carbon actually crystallized in the form of black and transparent diamonds. Treatment of the regulus with various acids dissolved away all the other materials so that the diamonds and the silicon carbide, formed at the same time, were left behind. These were separated by virtue of their divergent densities, only the diamonds sinking in methylene iodide.

The first communication of these findings was made to the Académie on February 6, 1893. The report soon reached the daily press and made the name Moissan extremely popular. The news that the precious stone could be prepared by a relatively simple process aroused fear or pleasure, depending on whether the reader actually owned diamonds or hoped to. However, the day of cheap diamonds of gem quality has not arrived even yet. Repetition of the experiment by Moissan himself (1894, 1896, 1905) and by others (Crookes, 1894; Majorana, 1896; Ludwig, 1901) invariably gave extremely low yields. They sufficed merely to prove that the diamonds yielded carbon dioxide when burned. Furthermore, the artificial diamonds, which were mostly black, and hence comparable to the naturally occurring carbonado, were minute. The largest obtained by Moissan was a colorless specimen 0.7 mm. long. In his laboratory it was called "Le Régent" after the famed brilliant in the Louvre.

In connection with his studies of diamonds, Moissan published also a whole series of observations on amorphous carbon (1895, 1902) and graphite (1894, 1895, 1897). He resumed his work on diamonds shortly before his death, employing improved apparatus.

Moissan's other researches with the electric furnace were of more importance to chemistry than his manufacture of diamonds. The first model of the *four électrique* which he used was quite small. It consisted of two pieces of lime, the upper serving as the cover. The lower piece was hollowed out so as to accommodate a 2-cm. carbon crucible containing the material to be heated, and two channels for the introduction of the approximately 1-cm. carbon electrodes, between which the arc was produced directly above the crucible. According to his collaborators, Moissan had contrived this furnace (1892) himself, without knowing anything of the various electric furnaces which had already been described in the literature and which were already in technical use. Davy (1810) and Pepys (1815) had used electricity as a source of heat; but practical importance had to await the means of producing stronger currents. Many forms of electrical furnaces were known before 1892. The so-called Moissan furnace was not really new; Pichon, Siemens, and Rogerson had previously described furnaces employing indirect heating by means of an arc. However, it would not be proper to deny him credit on such historical grounds. He had selected a furnace design which suited his experiments, one that was easy to construct and manipulate, one that eliminated all electrolytic action by the current and thus provided the best possible insight into the thermal reactions taking place in the furnace. He used this furnace with such skill that Moissan is generally regarded as the founder of high temperature chemistry, even though some of the reactions were discovered before him or independently of him. There is no doubt that his researches also contributed indirectly but definitely to the future technological advances in this field.

This little furnace was operated for the first time in June, 1892, in the École de Pharmacie. A small dynamo delivered the current of 40 volts and 45 amperes. Although interesting results were obtained, this apparatus was soon found inadequate. His slogan be-

came "More heat." To have more powerful currents available, he successively carried out his experiments in two other schools and at two electric power stations. Finally in 1900 an electric furnace was set up in his own laboratory. Its dimensions were much greater than his first model. Since large blocks of lime could not be obtained, he now constructed the furnace of limestone. The diameter of the carbon electrodes was 5 cm.; the graphite crucible had a capacity 100 times that of the original. If substances were to be heated in a particular atmosphere, the reaction was carried out in a carbon tube which passed through the furnace close to the arc. In some experiments, such as the preparation of titanium or the volatilization of carbon, the current consumption reached 2200 amperes at 80 volts. According to measurements by Violle, 3500° could be attained. Of course the temperature was much less than this in most of the experiments. It was shown that some of the reactions conducted in the electric furnace occur at 2000° or less.

In the application of the electric furnace Moissan had found an area which suited his tastes exactly. High temperature chemistry was a virgin field which yielded new facts and new compounds at every step, without requiring the previous preparation of the soil by modern theories or physiochemical methods. The concept of "the nonvolatile materials" was dispelled, just as fifteen years before the idea of "nonliquefiable gases" had been shown to be untenable. It was easy to prepare metals that had not been isolated previously; materials such as carbon, silicon, and boron, which were inactive at ordinary temperatures, reacted with almost all elements and formed carbides, silicides, and borides, of whose very existence practically nothing had hitherto been known. The results he had obtained thus far were compiled in his "*Le Four électrique*," a book of 400 pages published in 1897.

Moissan's studies of the metal hydrides were fruitful. These compounds had previously been rather rare and were considered to be alloys of "metallic hydrogen." Strangely enough, the crystalline lithium hydride, LiH , observed by Guntz in 1893, had received hardly any attention. Moissan prepared CaH_2 , NaH , KH , RbH , and CsH from hydrogen and the respective metals (1898–1903). These compounds looked like salts rather than alloys; they did not conduct an electric current. They proved to be very reactive;

most of them ignited spontaneously when exposed to the air. If warmed with ethyl or methyl iodide, they yielded ethane and methane, and at room temperature they reacted with sulfur dioxide to give hydrosulfites, e.g., $\text{K}_2\text{S}_2\text{O}_4$. Acetylene reacted with them to yield acetylene metal carbides, and carbon dioxide with hydrides produced formates. The reaction between hydride and carbon dioxide, which at higher temperature yielded oxalate as well as formate, was found to be greatly influenced by water vapor. If moisture was excluded, potassium hydride and carbon dioxide did not react below $+54^\circ$, whereas the reaction occurred even at -80° provided the carbon dioxide had been passed over ice at -85° .

Moissan remained professor of toxicology at the *École de Pharmacie* for thirteen years. In 1899 he was appointed successor to Riche as professor of inorganic chemistry, which actually he had been all along. At the close of 1900, he was made a professor in the *Faculté des Sciences* at the University of Paris and took over the laboratory previously headed by Troost. He took a leading part in preparing the plans for the new chemistry section at the Sorbonne, but he died before they were realized.

In 1899 when the present writer came to Paris to work for a time with Moissan, he had just recently taken over the Riche laboratory. The *École de Pharmacie*, on the beautiful Avenue de l'Observatoire, was very attractive when viewed from the outside; the vestibule was adorned with mural paintings. The picture altered when the laboratories came into view. There was little light or space. Moissan's laboratory was on two floors. In one he himself worked along with one or two assistants; the rest of his collaborators were housed below on the ground floor. An international flavor permeated the atmosphere. In addition to several Frenchmen, there were at that time two Germans, an American, an Austrian, an Englishman, and two Norwegians who had come to learn his methods, particularly how to manipulate the electric furnace. The common language was German, which all understood very well with the exception of the Frenchman. In later years, Moissan continued to attract foreign students.

The most striking thing on entering the Moissan laboratory was its scrupulous cleanliness, which gave the lie to the old witticism

that chemistry is the dirty part of physics. The wood floors were waxed every Saturday. Several days after the writer's arrival, Moissan was making his rounds through the room in which we were working. He suddenly took a look at the floor and asked: "Who did that?" Only then did I discover that this inquiry had been occasioned by a few drops of water from my wash bottle. We ordinarily spoke to Moissan rather seldom, but he kept himself well-informed about the progress of our work. The intermediary was usually Lebeau, who had been his assistant since 1890. Amiability was one of Moissan's fundamental characteristics, and with it he charmed everyone who came in contact with him. He had practically no personal enemies.

Although he spent much time in the laboratory, Moissan never lost his interest for nonchemical matters. He read almost every important piece of the current French literature and was an ardent collector of paintings and engravings. His special pride was several Corot landscapes which hung in his home on the Rue Vauquelin. He had an extensive collection of autographs from the period of the French Revolution. He was keenly interested also in technical questions and matters concerning the national economy. On his many trips he sought to gain a basis for forming his own opinion on such matters.

Moissan was considered one of the best scientific lecturers in Paris. To hear him was a real aesthetic pleasure, and his discourses were a welcome opportunity for foreigners to strengthen their knowledge of the French language. Without using much external effort—his slender, rather large, figure produced a more tranquil impression while lecturing than in face-to-face conversations—he held his audience through his clear exposition and the elegant, often humorous, form in which he presented his subject matter, an impression that was heightened by the pleasing tone of his voice.

The course of lectures on inorganic chemistry opened with an introduction to the entire field of chemical operations and theories, presented in a manner that made high demands on the acquisitive talents of the listeners. Many demonstrations were a feature of these lectures. The subsequent discussion of the individual elements was accompanied by not too many experiments, but these

had been carefully planned and required considerable apparatus, and they were carried out by his assistants. Moissan himself confined his attention almost entirely to the lecture. He was popular with the students, but nevertheless at times they behaved in a rather unseemly manner. The only seats in the auditorium were crude, low benches without numbers—no writing surfaces were provided. There was always a race to get the front places. At precisely 5 o'clock, the two doors at the top of the steep stairs were opened simultaneously by the janitors, and like a horde of savages, the students, who had been waiting a long time, rushed down the stairs; the women, with flying skirts, usually in the vanguard. The 15-minute interval before the lecture began was ordinarily filled by singing songs, mostly political in nature, and punctuated by stamping on the floor.

The general recognition which Moissan's personality and scientific achievements enjoyed were reflected in the many honors he received. In 1900 he was made *Commandeur de la Légion d'Honneur*. He was a member of almost all of the eminent academies and chemical societies. He was awarded numerous prizes including the Nobel Prize for Chemistry (1906). He was particularly pleased with the medal that was commissioned by his students and friends and handed to him in December, 1906, on the twentieth anniversary of the isolation of fluorine.

He could hardly look forward to more honors. The finest reward for which he hoped was the privilege of continuing his chemical career. He had no intention of resting on his laurels. In a speech he once declared: "We, all of us, should set our ideal so high that we can never attain it."

However, his plans for the future were made in vain. When he reached home from the laboratory on February 6, 1907, he suffered a severe attack of appendicitis. It yielded to treatment, but a recurrence on February 16 made an operation imperative. The operation was successful but the heart condition from which he had been suffering for some years was greatly intensified. He had come to realize in his later years that he had not taken enough care of his health. He once confessed: "Fluorine has taken ten years of my life." Death came to him on February 20, 1907. Thus

HENRI MOISSAN

closed this sunny life which shed so much light on science and gave so much warmth to his friends.

NOTES AND REFERENCES

Paul Lebeau, "Henri Moissan et Son Oeuvre," Institut de France, *Acad. sci., Paris*, Palais de l'Institut (1955).

F. P. Bundy, H. T. Hall, H. M. Strong, and R. H. Wentorf, "Man-made Diamonds," *Nature*, 176, 51 (1955).

From: *Ber. deut. chem. Ges.*, 40, 5099-5130 (1907), abbreviated.

Translated by Ralph E. Oesper.

ALFRED STOCK

.. 68 ..

Emil Fischer

1852-1919



EMIL FISCHER was born on October 9, 1852, at Euskirchen, a small town not far from Cologne. The family was Protestant and had been in the Rhineland since the end of the seventeenth century. His father, with little formal education, nevertheless had become a successful business man. He made a name for himself in the community and was in comfortable circumstances at a fairly early age. The mother, nee Poensgen, came from a family that is still well known in Rhenish industrial circles.

The boy had a pleasant youth; his playmates were mostly his numerous cousins. After three years with a private tutor, he spent four years in the local public school. Then followed two years at the gymnasium at Wetzlar and two years more at the gymnasium in Bonn. Emil was an excellent student; he had a fine memory and a quick grasp of all kinds of subject matter. His final examination was graded "with great distinction" when he, as *primus omnium*, graduated from school in the spring of 1869.

There was some difficulty about choosing a career. In line with the family tradition, his father wished to train him for the business world, so that Emil, the only surviving son (he had five sisters), could eventually become his successor. The youth preferred natural science, mathematics, and the exact sciences, especially physics. A compromise was reached and a trial period in business was begun. However, his dislike grew upon closer acquaintance with commercial matters, and his business tutor, his uncle and partner in the family lumber business, soon prophesized: "The boy will never amount to anything." Emil's father, conceding defeat, then consented to a university education. It is said that he clothed his decision in the declaration: "The boy is too stupid to be a businessman, so he had better become a student." However, he saw to it that chemistry was chosen as the field of study since it seemed likely that at least it would provide a living. The start of his higher education had to be delayed, since the eighteen-year-old youth had contracted a persistent gastric catarrh, and this had to be definitely cured before he could leave home.

He enrolled at the University of Bonn in the spring of 1871. He had no financial worries either during his student years or later in his career. Thanks to his father, he was a well-to-do student. It is true that the start of his studies did not bring him much pleasure. He listened to the brilliant lectures delivered by August von Kekulé with great satisfaction. In contrast, the laboratory instruction, in which Kekulé had practically no interest, was rather old-fashioned and unattractive. Emil's predilection for physics was still dominant and it required the full persuasion of his cousin and fellow student, Otto Fischer (1852–1932), to keep him from leaving chemistry. Together they transferred to Strasbourg in the fall of 1872, where the university in the newly regained Alsace had been provided by the German authorities with distinguished teachers and ample resources. Analytical chemistry was taught in modern dress by F. Rose in both the theoretical and practical aspects. It was especially the young Adolf Baeyer—the future discoverer of the synthesis of indigo—who attracted the young student and finally aroused his enthusiasm for chemistry.

In accord with the prevailing custom, as soon as he had finished his training in analytical chemistry, the young man began his doctoral work. The thesis topic was suggested by Baeyer. Here once more there were difficulties; his first experiment had an unfortunate ending. A precious preparation, which had required weeks to make, was lost together with several kilograms of mercury in the cracks and joints of the worn floor when Emil stumbled while carrying a large flask. However, neither Fischer nor Baeyer was discouraged by this accident. Research was successfully completed in the field of phthaleins, a class of dyes discovered by Baeyer, and the doctorate was conferred in 1874. According to his own account, the oral examination was not too brilliant, which is not surprising since, following the former French custom, every member of the Strasbourg faculty was privileged to put questions to the candidate. The geologist, in particular, was not impressed with the answers he received from Fischer, who had not prepared himself in this field at all. However, Baeyer who had a talent for recognizing latent powers, sensed the special and great endowments for chemistry possessed by the fledgling Doctor Fischer and immediately offered him a post as his assistant.

Fischer made his first great discovery while still at Strasbourg, that of phenylhydrazine. In his hands this compound later became an important reagent for his own researches, and it was an integral link in the synthesis of antipyrine, a successful febrifuge, carried out by his own student and friend Ludwig Knorr (1859–1921). The discovery of phenylhydrazine was in itself an accident, and it offers a prime example of how unexpected findings, that seem unfortunate at the time, can often lead to significant successes. The logical follow-up of what initially appeared to be an unsuccessful student experiment eventually led to this achievement.

In 1875, Baeyer accepted a call to Munich as successor to Justus von Liebig. He persuaded his young assistant, who had already earned his spurs, to accompany him to the Bavarian capital. In the fall of 1875, Fischer took over the assistantship in the organic division of the chemistry department.

He had spent seven semesters in Strasbourg. In addition to his training in chemistry, which occupied most of his time and attention, he had diligently studied physics under August Kundt and his assistant, Wilhelm Röntgen, and mineralogy under Paul Groth. However, the initial urge to change to physics had vanished. Baeyer's influence had swept the board. Fischer later declared that next to his father he owed to this teacher most of what he had accomplished in his life.

In Munich, Fischer and a number of his collaborators worked on the newly discovered hydrazines. At this university it was still the custom to recognize the doctorate from another school only after a local oral re-examination, the so-called *nostrification*; Baeyer lowered this hurdle for his assistant by quizzing him only about hydrazines, a field that of course was far better known to its discoverer, Fischer himself, than to any of his examiners.

At the insistence of Baeyer, Fischer qualified as *Privatdozent* in 1878. The assigned theme of the qualifying lecture was: "The present problems of chemistry." The candidate was given three days for preparation. Fischer was no born orator. Carefully writing down the text of the lecture was a necessity for him on all occasions. But by virtue of his excellent memory he was then able to deliver the speech freely and literally, without ever once referring

to the manuscript. His speeches and lectures thus gave the impression of being freshly conceived and full of life. Moreover, until his last years, his very keen and impressive eyes were always directed to his audience so that every listener had the feeling that he was being spoken to individually.

His cousin Otto Fischer had followed him to Munich, and shortly before Emil's qualification they collaborated in a new field. Synthetic organic dyes had become of great interest to the chemical industry as well as to the consumers. The first of such coloring matters prepared from coal tar had been discovered through purely empirical methods. Their structure and constitution were still unknown. A. W. Hofmann, the brilliant head of chemistry at the University of Berlin, evolved a theory of the constitution of these dyes. Through their convincing experiments, Emil and Otto Fischer proved that a second theory was correct as regards another class of dyes, namely, the derivatives of triphenylmethane. This success contributed fundamentally to the further technical development of these artificial dyes, and their discoverers became widely known.

On the basis of this success, and because of a half-year's training under F. Rose at Strasbourg, Emil Fischer received the associate professorship in analytical chemistry at Munich in 1879. He retained his interest in organic chemistry, of course, but also took intense interest in the young chemists working in his division and their analytical researches. He spent the entire day from 8 to 6 in the laboratory and postponed the usual big meal from noon to the evening. His lectures were popular among the students, even though at first his rather unfamiliar Rhenish dialect created considerable difficulties among the Munich students.

In the meantime, his father had become reconciled to his son's choice of profession and, proud of his successes, bequeathed to him a sum that made him financially independent. Consequently, having no need to worry about money, Emil Fischer was able to devote himself entirely to his scientific activities and academic career, which in those days was still less lucrative for young professors than now. Actually, at twenty-seven, Fischer was in a position to refuse his first call to a full professorship (at the Technical Uni-

versity of Aachen) because he did not wish to leave the inspiring circle then active in the Munich laboratory.

However, two years later he accepted an appointment to the chair in chemistry at Erlangen. His new facilities consisted of a somewhat smaller chemistry building which required only a few necessary improvements, particularly the installation of an adequate ventilation system for the laboratories. To the former fields of his research he now added a new line, entering for the first time the border region between chemistry and physiology, namely, the chemistry of the purine compounds. These included the active materials contained in coffee, tea, and cocoa, i.e., caffeine (or theine) and theobromine, which in the course of time were found to be physiologically very important components in the cell nuclei and in the nucleic acids. Together with a number of capable younger associates, Fischer explored a whole series of compounds in this field with respect to their constitution, established their structure, and eventually accomplished their synthesis. The brilliant discovery of antipyrine, by Knorr, who had followed Fischer from Munich, occurred at Erlangen.

Fischer's successes had brought him to the attention not only of the scientific world but also that of the chemical industry. A number of his students were doing excellent work in industry. In 1883, the Badiſche Anilin- und Soda-Fabrik asked Fischer to take over the direction of its scientific laboratory, a post formerly held by Heinrich Caro (1834–1910). The offer was tremendously attractive from the salary standpoint and because of the much greater facilities available for research. None the less, Fischer refused to sacrifice the freedom provided by his academic surroundings, advantages which still form the most important basis of university teaching and research. His independent financial status doubtless made the decision much easier.

The last part of his Erlangen period was darkened by a serious illness. An obstinate chronic catarrh, which also attacked the intestinal tract, forced him to take a year's leave of absence. For the second time in his life, this serious ailment warned the young man not to overexert himself. From that time on he lived more carefully and worried excessively about simple colds that others

passed over without much thought. It was his state of health that also caused him to refuse the flattering offer from the Federal Technical University of Zurich, where he would have succeeded Viktor Meyer.

Soon after he had resumed his duties he received a call from the University of Würzburg. The Würzburg authorities, who were aware of his illness, had made certain of his recovery before sending him this offer. One of the Würzburg faculty, the aged zoologist Semper, called on Fischer in Heidelberg where he was visiting and enticed him to ascend the Heidelberg hills and drink champagne together. Fischer came out of this examination in much better shape than the examiner, who reported back to his colleagues that "the candidate is completely healthy and probably will outlive all of you."

In comparison to Erlangen, Würzburg was tempting. It offered a wider professional scene of action, the faculty contained a number of especially inspiring colleagues in various fields, who awaited with open arms the now eminent young chemist. The city and its surroundings were much more attractive than Erlangen. Fischer accepted the call, but with open eyes. The rather old chemistry building had to be renovated, particularly by installing effective ventilation, and in addition a new building was promised in the not too distant future. Actually this was constructed by his successor, Otto Fischer, according to the plans drawn up by Emil Fischer. Nevertheless, Fischer counted his seven years at Würzburg among the happiest of his career. He enjoyed the city and its surroundings, the magnificent location on the Main in the midst of a fruitful hilly landscape, and the civic and ecclesiastical structures, in which German baroque had reached its peak. Since the city was not too large, a more intimate relationship was possible between the professors and students, and its development was favorably reflected in their scientific activities. Although a Protestant, Fischer was on very friendly terms with a number of the representatives of the Catholic theology, a fine feature of the tolerance that distinguished life in Würzburg at that time, which appealed greatly to Fischer, who abhorred all intolerance of religious and political faiths. By express order of the Bishop of Speyer, twenty-five Catholic theologians regularly attended Fischer's

lectures so that they might be able to bring to the members of their congregations some understanding of the activities in the great chemical works of the Palatinate, particularly the Badische Anilin- und Soda-Fabrik, where many of the parishioners were employed.

A group of capable young chemists soon gathered around Emil Fischer. Ludwig von Medicus was already in Würzburg as professor of applied chemistry. Knorr and Hermann Reisenegger soon followed from Erlangen. Others included Wilhelm Wislicenus, Julius Tafel, and Oskar Piloty.

A definite change of Fischer's personal life occurred during this time. Years before he had accidentally become acquainted on the train between Munich and Erlangen with the Erlangen anatomist Gerlach and his daughter Agnes. Obviously a personable full professor, only thirty-two years old, would constantly be subject to attacks on his bachelorhood, but hitherto all such campaigns, especially by the faculty wives, had been fruitless. He himself once had written that "he had definitely decided to travel his life's path alone." However, this resolve seems to have become weaker at the start of his Würzburg period. In 1885 he closed a letter to Baeyer: "My best regards to your wife and tell her in all secrecy that I wish I too had one." His marriage to Agnes Gerlach ushered in an all too brief period of happiness for Fischer. She seems to have been a very attractive and lovable woman. His father was delighted with her when the young couple visited Euskirchen, and there are many other evidences of her beauty, her kindness, and her understanding care for her husband. They had three sons. Unfortunately, only seven years after their marriage, she died of a middle-ear inflammation.

Thanks to the happy domestic atmosphere, and especially because at this time of his life he derived particular joy from his achievements, the years in Würzburg represented a peak in his career. First the studies of the purine derivatives were continued and extended to related compounds. They led—later in Berlin—to a well-rounded picture of this important field. Especially important and successful were the investigations carried out in Würzburg on the simple sugars. Their structures, on broad lines, were already known, but the numerous cases of isomerism were still to be elucidated. Tenacious and painstaking steps finally enabled

him to reach the complete application of the theory of the asymmetric carbon atom to this field and to untangle this complicated subject. At almost the same time he began the synthesis of the simple sugars, which reached an imposing apex in the synthesis of mannose, fructose, and glucose. On June 23, 1890, at a special meeting of the German Chemical Society he gave a comprehensive report on the status of carbohydrate research. It must have been an unusually fascinating lecture. Even so keen a critic as Carl Harries wrote: "I have never heard a better lecture with respect to form and content, filled with enthusiasm and genuine moderation; in it the truly great investigator came clearly into view. Emil Fischer became for us the yardstick by which to measure all other personalities."

When A. W. Hofmann died in the spring of 1892, the Berlin faculty suggested as possible successors Kekulé, Baeyer, and Emil Fischer. Negotiations were successfully concluded within two months after Baeyer stated that he would not leave Munich. It probably was not easy for Fischer to decide to leave Würzburg and take over at Berlin. He was only forty when he assumed the most important chair of chemistry in Germany. One of the principal promises made to him by the ministry was for a new chemistry building. The structure on Georgenstrasse, built by Hofmann when he went to Berlin from London in 1865, was no longer adequate for the ever-increasing teaching and research demands. However, it was almost eight years before the new building on the Hessische Strasse could be occupied. The negotiations conducted by Fischer in his customary insistent and tenacious manner with regard to planning this large project earned him the respect, recognition, and eventually the friendship of Privy Councillor, Friedrich Althoff, the influential Prussian Minister of Education. The great chemical industries had also taken a hand in these tedious negotiations, especially with the Prussian Ministry of Finance. For many years this laboratory structure was a model in the efficient arrangement of its rooms.

In Berlin, the researches were continued on the two main topics that had occupied his attention during the last years. The chemistry of the purines was brought to a certain degree of completion. The field of carbohydrates was widened and extended

primarily to the glycosides, the oligosaccharides, and the glycoside-splitting ferments (enzymes).

His work on the purines and carbohydrates won world-wide recognition and brought him the Nobel prize in 1902. It was the second such award in chemistry. When closing his remarks on this occasion the president of the Swedish Academy of Sciences said: "The special method of investigation which characterized organic chemistry during the past decades has found its highest development and finest form in Fischer's sugar and purine researches. They can be classed as being without superiors from the experimental standpoint."

Later, Emil Fischer brought these two fields together. The *N*-glycosides of the purines and pyrimidines occur in the nucleic acids, which are the building units of the nucleins. The first model experiments leading to the synthesis of definite nucleosides from sugar and purine—or pyrimidine—derivatives were carried out and nucleoside-like compounds were obtained by condensation with phosphoric acid.

His success in these two fields gave Fischer such confidence in the methods of organic chemistry that, after the first years in Berlin, he turned to a new topic, namely, the proteins. He began with the simple and feasible. In his synthesis of the sugars he had found several methods of resolving racemates into their optically active components. The simplest of the then known building units of protein, the amino acids are—with the exception of glycocoll—asymmetrically constructed. The material obtained by synthesis separates in the racemic form and, to be comparable to the natural product, must be resolved into its optically active components. The first amino acid studies, i.e., the first of Fischer's protein researches, dealt with the resolution of the synthetic optically inactive amino acids into their optical antipodes. As a supplement to these studies, Fischer sometime later investigated the application of the Walden inversion in the synthesis and transformation of the amino acids. He showed that this kind of substitution is much more prevalent than had been suspected.

In 1901, Fischer for the first time prepared the esters of the amino acids and stressed the fact that they can be distilled. This was an extension of work that had been initiated some ten years

earlier by Theodor Curtius. Glycyl-glycine, the first simple dipeptide synthesized by Fischer, was described in 1901 in collaboration with Ernest Forneau. This same year also saw the publication of the first hydrolysis of casein with subsequent ester formation and fractional distillation.

These protein investigations were continued on a large scale for years. Amino acids that occurred in nature were prepared in the laboratory and new examples were discovered. The synthesis of the oligopeptides was extended and reached its peak in octodeka-peptide, which had many of the characteristics of a natural protein. The analysis of protein hydrolysates was accomplished, with the collaboration of Emil Abderhalden, through the fractional distillation of the esters and led to a more precise understanding of the composition of the proteins.

Other areas of investigation were added in time. Following a visit by The Svedberg, the noted Swedish authority on colloids, Fischer attempted to prepare what for that time was regarded as a "high-molecular" but well-defined product. This iodophenylosazone of an arylidisaccharide had a molecular weight of more than 4000.

The ferments (enzymes) also engaged his attention in connection with his studies of carbohydrates and proteins. He was one of the first to emphasize the specificity of ferments and expressed this fact in the oft-quoted declaration: "A ferment fits its substrate as a complicated key its lock."

His frequent vacations in the Black Forest led him to an additional field of study. The large old evergreens there are often heavily festooned with lichens, and he became interested in the chemical substances contained in the latter. This study brought him, via the polyesters of phenolcarboxylic acids, to the "depsides." In close connection with these studies was an investigation of the tanning substances. Eventually they were found to be sugar derivatives of gallic acid and similar phenolcarboxylic acids.

Finally, in his last years he turned his attention to the fats. Although these researches were not completed, his study of the simple esters of glycerol produced an important finding: the acyl wandering in esters of aliphatic polyhydroxyl compounds, which had already played a part with respect to the polyphenols in the study of depsides.

His position in Berlin brought him many responsibilities and duties. He served several times as president and vice-president of the German Chemical Society. He was a member of the Prussian Academy of Sciences, and as such looked after the interests of chemistry, but also cooperated along other lines. For instance, despite vigorous opposition, he successfully campaigned for the granting of a large sum to defray the costs of a solar eclipse expedition whose main object was to test the theory of relativity.

He seldom took part in the work of the faculty of the university, but on the rare occasions when he was interested he knew his goals and usually gained his objective especially when the matter at hand involved the summoning of eminent scientists to become professors.

However, it became increasingly difficult for him to find the time for these outside activities without slighting his teaching and research duties. Thus he constantly sought to find some relief from the routine teaching by turning over to younger men first the main demonstration courses in organic chemistry and then those in inorganic chemistry. But even then he found that the academic teacher expends far too much time and energy on these extracurricular matters to the detriment of his most important duty, i.e., his research activities. These thoughts were largely responsible for his active and fruitful participation in the founding of the pure research laboratories under the auspices of the Kaiser Wilhelm Gesellschaft. One of the first of these was the Kaiser Wilhelm Institut für Chemie, built at Dahlem in the outskirts of Berlin in 1911. He took an active part also in the founding of the Kaiser Wilhelm Institut für Kohlenforschung at Mühlheim, which was completed in 1914 just prior to the outbreak of World War I. The scientific accomplishments of these research institutions, which were joined eventually by others devoted to various fields, proved the wisdom of the basic idea which he had so ardently advocated.

Although Fischer limited his own scientific endeavors to certain fields of chemistry, he never lost sight of the importance of other topics. A number of nonorganic eminent chemists were trained in his Berlin institute and the researches carried on there were not restricted to organic subjects. Franz Fischer, the discoverer of the

Fischer-Tropsch synthesis of hydrocarbons and Alfred Stock, the well-known inorganic chemist, are typical examples. Emil Fischer early sensed the significance of radioactivity. He provided working space in his Berlin laboratory to Otto Hahn and Lise Meitner until they, through his influence, moved into the newly erected Kaiser Wilhelm Institut für Chemie.

World War I was a heavy blow to Emil Fischer. His research activities were curtailed and conducted only with great difficulty. He not only endured the general results of the war and the German defeat but lost two of his three sons.

After the close of the war, the research activity was resumed at an increased pace. But cancer, that dread malignant disease which he himself had once tried to vanquish by chemotherapeutic means, attacked him. When the diagnosis was confirmed he put his house in order. But his will to live was gone. He died on July 15, 1919; his grave is in Wannsee near Berlin.

Scientific accomplishments, planned and carried out with far-seeing objectives, but firmly rooted in carefully executed small studies, an unswervable love of truth, which invariably submitted to the experimental findings no matter how seductive the theory, a keen understanding and an artistic intuition in minor as well as major occasions, reveal the great chemist in Emil Fischer. His comprehension of other problems in chemistry and the natural sciences and his entire personality make him one of the truly great German scientists. As stated by Richard Willstätter and echoed by all who knew Emil Fischer and his work:

He was the unmatched classicist, master of organic-chemical investigation with regard to analysis and synthesis, as a personality a princely man.

NOTES AND REFERENCES

- Emil Fischer, "Aus meinem Leben," Verlag Julius Springer, Berlin, 1921.
 Kurt Hoesch, "Emil Fischer. Sein Leben und sein Werk," Verlag Chemie, Berlin (now Heidelberg), 1921.
 Burckhardt Helferich, "Emil Fischer," *Deutsches Biographisches Jahrbuch*, 2, Überleitungs band, Verband der Deutschen Akademien, Berlin, 1917-21.

EMIL FISCHER

Burckhardt Helferich, "Emil Fischer, sein Leben und seine wissenschaftlichen Leistungen," Festschrift der Stadt Euskirchen, 1952.

Burckhardt Helferich, "Emil Fischer zum hundertsten Geburtstag," Z. angew. Chem., 65, 45-52 (1952).

Translated by Ralph E. Oesper.

BURCKHARDT HELFERICH

.. 69 ..

Sir William Ramsay

1852-1916



THE name of Sir William Ramsay calls to mind at once, with all their meaning, two capital discoveries, to some extent paradoxical: On the one hand, the existence in the atmospheric air of a series of gaseous elements, which their chemical inertness relegates to the very borderland of chemistry; on the other hand, the production of one of these gases, helium, by the spontaneous disintegration of the radium atom, two classes of facts essentially new and of fundamental importance, whose discovery was possible only to an investigator of the highest rank, capable through exceptional ability, natural or acquired, of bringing light into the darkness of the unknown.

Of Scotch origin—he was born in Glasgow in 1852—Ramsay's hereditary influences were most favorable. In his family were chemists and doctors of note, and one of his uncles, Sir Andrew Ramsay, was a well-known geologist. Thus, as he himself liked to recall, Ramsay was descended from ancestors well above the average intellectually and in scientific pursuits, and he was well aware that he owed to them his calling and his ability as a chemist.

Having begun his studies in his native city, Ramsay went to complete them in Germany, at first at Heidelberg, with Bunsen, and afterwards in Tübingen in the Fittig laboratory, where after some researches on the ammonia compounds of platinum, he studied the toluic acids. Organic chemistry attracted him by the flexibility of its combinations and the ingeniousness of its structural theories. On his return to Glasgow, where he secured a post as assistant, he studied specially the pyridic group, doubtless attracted by the problem of the synthesis of the cinchona alkaloids.

In 1880, at the age of twenty-eight, given the title of professor of chemistry at the University of Bristol, Ramsay began, in collaboration with his assistant, S. Young, a series of works on physicochemistry which were not slow in being noticed. They had for an object the revision of the physicochemical properties of a certain number of liquids, water, alcohols, ethers, hydrocarbons, etc., with

a view especially of determining exactly the relation of these properties to the atomic or molecular weights.

For the execution of so many delicate researches, all kinds of new apparatus had to be designed and constructed, with the result, extremely fortunate for his following career, that Ramsay became a very adroit blower of glass. Many of these contrivances are in everyday use in laboratories.

It was in 1887 that Ramsay was called to the University College at London, to succeed Williamson in that chair of chemistry already renowned, which he was by his efforts to make shine with a great light. For thirty years in fact, Ramsay was to display in this post of honor the most fertile and brilliant activity. His peculiar qualities as an experimenter and his originality stood out in striking relief in a work which he published in 1893 in collaboration with Shields. Following a remarkable series of researches on surface tensions and densities at different temperatures, Ramsay gave to science the first experimental method of determining the molecular weights of substances in a liquid state.

We shall leave here various other works, of a special nature, in order to come without more delay to those researches which were to immortalize the name of Ramsay.

In 1894 Ramsay was forty-two years of age. His work was already considerable in amount and his reputation solidly established, but he could not yet be called a celebrity. In possession of scientific knowledge as profound as it was extensive and varied, a penetrating mind with broad vision, a philosopher mindful of the general movement of the sciences, and eager to solve the mysteries of nature, free from all dogmatism and with mind open to even the most daring conceptions, an experimenter of finished technique, an enthusiastic spirit, Ramsay was ready for epoch-making discoveries. Given a favorable occasion, his genius would be fully equal to the task. Here is the occasion.

As often happens in scientific research, a chance observation may lead to the most unexpected results. Lord Rayleigh, who for several years had pursued with meticulous care the determination of the density of the principal simple gases (hydrogen, oxygen, nitrogen), noticed that the density of the nitrogen extracted from the air through absorption of other known gases was always greater

than that of chemical nitrogen, coming from different sources—oxides of nitrogen, ammonia, urea, etc. The difference affected the third decimal and did not exceed one-half per cent, but it was certainly more than experimental error.

Three hypotheses could explain this irregularity. The atmospheric nitrogen might be constituted in part of complex molecules of nitrogen comparable to the oxygen compound called ozone. Conversely, in the chemical nitrogen a certain proportion of the molecules might be dissociated into free atoms. But the density of neither of the gases, after being kept for eight months, underwent any change, and the permanent existence of condensed nitrogen or of dissociated nitrogen (atomic nitrogen) would scarcely be likely. Lord Rayleigh, who had at first accepted these explanations, rejected them to adopt the third hypothesis, according to which the atmospheric nitrogen is constituted of a chemical nitrogen mixed with an unknown gas of greater density. Being consulted by Lord Rayleigh, Ramsay was of the same opinion, and the two scholars at once united their efforts to isolate the mysterious gas whose existence was thus revealed.

It is interesting to recall here that in the fundamental experiments in which Cavendish, a century before, had established the formation of nitric acid by the prolonged action of electric sparks on a mixture of oxygen and nitrogen in the presence of moisture, the celebrated English chemist had noted that even after a very long time there always remained, after absorption of the oxygen in excess, a small gaseous residue representing about one one-hundred-and-twentieth of the volume of nitrogen. But the observation has passed unnoticed, and until the researches of Lord Rayleigh, the nitrogen in the air had been considered as a simple gas, identical with "chemical nitrogen."

While Lord Rayleigh, taking up again the experiments of Cavendish, verified the fact that atmospheric nitrogen does indeed leave, after the action of the oxygen and the spark, a residue which could not be overlooked, Ramsay attacked the problem by a purely chemical method, that of absorbing the nitrogen by magnesium at red heat. The repeated action of this metal increased the density of the gas. From 14, its weight in relation to hydrogen, the density increased little by little to become fixed in the neighborhood of 20.

What remained was a new gas, absolutely distinct from nitrogen, characterized, aside from its density, by a peculiar spectrum very rich in lines in all regions and, a fact without precedent, by absolutely no ability to combine with any other substance whatsoever.

At the British Association meeting at Oxford in 1894, at the memorable session of August 13, Lord Rayleigh and Ramsay announced in turn that the nitrogen of the air is not pure nitrogen, and that it contains a small proportion of a gas more dense and much more inert, to which they gave, on account of its chemical inertness, the name of argon (α priv.; $\epsilon\rho\gamma\omicron\sigma$, energy). This communication caused a great sensation among the audience, and the daily press took up the matter at length.

But chemists are generally conservative, and although the discovery was affirmed by two scholars so well-qualified, many remained incredulous. It was not certain that argon was a simple substance. The molecular weight, according to the density, being 40, it might be a form of nitrogen cyanide CN_2 ; it was noticed also that a triatomic molecule of nitrogen N_3 would have a weight of 42, a figure not far from the one given above.

A few months sufficed for Ramsay to clear up the question and dissipate all doubts. The comparison of the specific heats at a constant volume and at constant pressure shows an equally unexpected fact—that the molecule is monatomic, and consequently the new gas can only be an element.

To find in the air a new gas, and, in addition, one of absolute chemical inertness, is indeed a truly great discovery. It brought at once to the authors a deservedly great renown. Ramsay was not slow in adding to it through other researches not less surprising. And it was here again that a fortunate opportunity presented itself to him; he exploited it with admirable and masterful decision.

Early in 1895 Ramsay learned, through a letter from Sir Henry Miers, that Hillebrand, chemist in the United States Geological Survey, had observed, while treating a uraniferous mineral, cleveite, with boiling sulfuric acid, the giving-off of a gas which appeared to him to be nitrogen. The effect produced on Ramsay by this news was entirely characteristic of his scientific temperament. Many chemists, while finding the observation interesting, would have put off the study of the subject until later, when they might have

more leisure. Ramsay, on receipt of the letter from Sir Henry Miers, called the laboratory aid and dispatched him immediately to the shops of the mineral merchants of London to buy all the cleveite that he could find. The cleveite arrived toward noon; before night it had been treated and the gas collected. During the two following days the known gases, except argon, which it had been expected would be found, were eliminated and the residue introduced into a spectrum tube. The spectrum of argon was not observed. There were few lines; one of these—yellow—was very brilliant. It was thought at first to be the line of sodium, present, perhaps, in the corroded electrodes. But Ramsay laughed at the idea; he was not in the habit of using dirty spectrum tubes, and, besides, he had made the tube himself. A comparison spectrum of sodium was observed simultaneously. The two lines were distinct and in no way superposed. It was then beyond doubt that it was a new gas, and the hypothesis was advanced that it might be helium.

Helium was that element, still unknown on the earth, whose existence in the sun was known through a spectroscopic observation carried out by the French astronomer Janssen at the time of the solar eclipse of the year 1868, and the subsequent suggestions of the English physicists Frankland and Lockyer. Was this new gas of Ramsay's helium, or was it not? The answer was not long in coming. The spectrum tube was sent to Sir William Crookes, who measured with great care the wavelength of the yellow line and found it identical with that of the solar line of helium. Scarcely a week had passed since Ramsay had received the letter from Sir Henry Miers.

At the general reunion of the Chemical Society in March, 1895, the discovery of terrestrial helium in the gases from cleveite was announced. Its molecular weight was 4, and a study of the specific heat indicated that the molecule was monatomic, like that of argon, which it also resembled through its complete chemical inertness.

During the two following years Ramsay hunted carefully for other sources of argon and helium. Argon and helium were found in certain mineral waters, those of Cauterets among others; today we know that they exist in all subterranean waters and gases.¹ Furthermore, helium can be derived from a series of rare minerals; this observation was of great interest in what followed, after it was

discovered that the same gas was given off in the disintegration of radium, as we shall see later on.

Their resistance to any combination assigned to argon and helium a place apart among the elements, and they did not fit in any of the groups of Mendeleeff's table. Ramsay boldly suggested that they constituted the first two known terms of a new group, characterized by a valence of zero. Secure in observed analogies in the other groups of the periodic system, Ramsay, in a communication to the meeting of the British Association in Toronto in 1897 with the suggestive title, "An Undiscovered Gas," predicted the existence of at least one other inert element, situated between helium and argon, near fluorine, and having an atomic weight not far from 20.

Before another year had passed, not only had Ramsay's prediction been realized, but more, in collaboration with Morris Travers, two other elementary inert gases had been discovered, whose places he also fixed in the periodic system, near bromine and iodine, with the neighboring atomic weights of 82 and 130.

Ramsay submitted to a close examination different thermal waters, such as those of minerals and of meteorites, without being able to discover any of the gases which he sought. Their presence in all the subterranean gases was to be demonstrated later,² thanks to the use of a method of fractionating by means of cooled charcoal inaugurated by Sir James Dewar.³

But if the three gases to be discovered really existed, ought they not to be found in considerable proportion in the atmospheric nitrogen along with argon? One hundred cubic centimeters of liquid air having been reduced through spontaneous evaporation to several cubic centimeters, Ramsay vaporized them in a gasometer, then eliminated from it the oxygen and nitrogen by appropriate means. The gaseous residue thus prepared furnished the spectrum of argon with, in addition, a yellow line and a very brilliant green line. Besides, the density was a little greater than that of pure argon; the residue examined was then argon mixed with a certain proportion of a heavier gas.

In order to isolate this gas, Ramsay aided by Travers, prepared 15 liters of argon, a task requiring several months, and liquefied it by cooling with liquid air. The clear liquid obtained was submitted

to a fractional evaporation very skillfully conducted, with the purpose of separating the gases more, or less, volatile than argon. The success was complete.

The first fractionation furnished a light gas, about ten times more dense than hydrogen, and characterized by a magnificent spectrum with brilliant lines in the red and the yellow. Ramsay called it neon. It is moreover accompanied by a certain proportion of helium, present also in the air, and from which it can be separated by the use of liquid hydrogen (-253°), which solidifies the neon and leaves the helium in a gaseous state.

The end products of the distillation of liquefied argon retained the two other new gases, which could, however, be separated by liquefaction and fractionating. Ramsay called them krypton and xenon; their densities in relation to hydrogen were 41 and 65.

For the three new gases, neon, krypton, and xenon, the study of the specific heats led, as for helium and argon, to a monatomic molecule. They are likewise chemically inert. Their atomic weights 20, 82, and 130 were found to occupy exactly the places indicated by the periodic table.

Thus, in the atmospheric air, which during more than a century had been believed to be perfectly known, Ramsay had succeeded, in the four years from 1894 to 1898, in isolating a complete natural group of simple gases. Indeed a splendid achievement. Striking proof of the fundamental truth comprehended in the periodic law. Witness, just as noteworthy, of the scientific faith and the ability in experimentation of this master. Nearly all the apparatus had to be invented, and Ramsay also had to construct most of it himself. Only those who have handled small quantities of gas and have prepared absolutely pure gases, giving spectra entirely free from foreign lines, are able to understand all the technical difficulties of such a work.

A little before the discovery of krypton, Ramsay thought he had isolated another element in the atmospheric argon; it had the same density as argon, but its spectrum was entirely different; he called it metargon and described several principal lines. Metargon was not, however, a new element; it was recognized that the lines indicated were due to traces of carbonic oxide, which occurs as an impurity in argon. Other chemists were working on the same prob-

lem, and Ramsay, too much hurried, had insufficiently purified his argon. I shall cite Ramsay himself in this connection:

Should we under such circumstances regret the publication of an error? It seems to me that an occasional error should be excusable. No one can be infallible; and besides, in these conjectures one has always a large number of good friends who promptly correct the inaccuracy.

It is certain that anyone may be deceived; but it is not anyone indeed who would have been capable of discovering krypton and xenon in the air, which contains, by volume, 1 in 20,000,000 of the first and 1 in 170,000,000 of the second.

This research on the rare gases of the atmosphere will remain a perfect model of original research. And if there was anything to be admired more than the ability in experimentation and the scientific penetration displayed, it was the energy and persevering ardor, qualities doubtless less brilliant, but which in this kind of work were absolutely indispensable.

Another question, in this connection, could not fail to present itself to Ramsay's mind. Are there not in the same group of inert gases, noble gases, as he liked to call them, other elements, heavier than xenon as predicted by the periodic system, or lighter than helium, such as nebulium, whose presence is probable in the nebulae and coronium, which appears to exist in the solar corona?

We shall recall in passing that, beside the inert gases, Armand Gautier recognized in the atmospheric air an appreciable proportion of a gas lighter than helium and which was not other than hydrogen, whose production proposed a most suggestive geochemical problem.

Ramsay busied himself then in the search for new rare gases. With Watson he examined the lightest gases in the atmosphere in the hope of obtaining a gas less dense than helium, but without success. He was not more fortunate in the systematic study, undertaken with Richard Moore, of the distillation products of an enormous mass of liquid air (120 tons), put at his disposal by George Claude. Ramsay arrived at the conclusion that if the air

contains gases heavier than xenon, the proportion of them is extremely small and does not exceed one twenty-fifth of one-billionth.

The discovery of the rare gases had excited universal enthusiasm. Physicists and chemists far and near wished to study these new elements; and it is interesting, for the glory of Ramsay, to indicate briefly the principal results that have issued from this study.

Some, interested especially in the problem of affinity, sought, but in vain, to arouse chemical activity which they supposed to be dormant in the rare gases.⁴ Others, on the other hand, sought for them in natural media. Following a systematic study of a great number of subterranean gases (gas from thermomineral sources, volcanic gas, fire damp), some simple conclusions have been formulated:⁵

(1) All the natural gaseous compounds contain the five rare gases, and certain of them contain appreciable quantities of helium, some as much as 6 per cent (thermal gas of Maizières, Côte-d'Or), and even 10 per cent (thermal gas of Santenay, Côte-d'Or). (2) The quantitative relation krypton-argon has practically the same value in all natural mixtures, the atmospheric air included; the relation krypton-xenon, different from the preceding, is likewise constant, as is also the relation xenon-argon, and the relations of these three gases with neon; it is possible to explain the constancy of the relations by the chemical inertness and the analogous properties of these gases, which have thus been able, since the time of the original nebulae, to come through free and mixed together and without their quantitative relations being sensibly changed, all the cataclysms of astronomy and geology. (3) Helium, it is true, accompanies the other members of the group on all their voyages, but it escapes all proportionality; and it could not be otherwise, inasmuch as only helium is produced continually from radioactive substances, and these are unequally divided in the different strata.

You see, gentlemen, what unexpected and weighty problems have been brought up by Ramsay's discovery. What an exceptional destiny is that of these five gases, whose chemical inertness has assured to them, since the beginning of time, an eternal inviolability, and has thus made of them, like the demigods, immortal

witnesses of all the physical phenomena of the earth and of the evolution of the spheres!

For what practical applications are the new elements destined? Lighting tests in neon have proved very encouraging. Argon is used in incandescent lamps. And above all—Ramsay himself made the proposition—balloons have been inflated with helium, and by this means made noninflammable.

We now come to the year 1902. Pierre Curie and Mme. Curie had just obtained radium, the magnificent completion of an admirable work begun by Mme. Curie in 1897, a little after the discovery of radioactivity by Henri Becquerel in 1896. It was a logical outcome that Ramsay was attracted toward these most interesting researches. The new domain thus opened to science had as yet been explored only by physicists; it seemed to him immediately that chemistry also could and ought to enter on the scene. He entered boldly on the subject; he was to make conquests in it of vast importance.

Frederick Soddy had come from Montreal, where he had been assisting Sir Ernest Rutherford in his beautiful work on thorium. The curious fact had been discovered that a material substance was continually given off from thorium; it was given the name of emanation. Actinium and radium also gave off an emanation. These new substances were evidently of a gaseous nature; and, with all the skill already acquired in the manipulation of small quantities of a gas, Ramsay found himself very well fitted to make a study of them. In collaboration with Soddy he tried to obtain the spectrum of the emanation of radium. As the amount of emanation which comes from even a relatively large quantity of radium is extremely small it was necessary to devise a special spectrum tube. It consisted of a thermometric capillary tube with an electrode made of a platinum wire soldered at the end, the second electrode being mercury, which was put in advance with the very small quantity of emanation with the aid of a pump. Traces of impurities prevented seeing the spectrum of the emanation until later; but what was the surprise of Ramsay and Soddy when, after the passage of sparks through the gas for some time, they saw appear, little by little, the lines of helium!

The discovery of Ramsay and Soddy was not slow in being

taken up; the formation of helium was demonstrated as coming from actinium by Debierne, from thorium and uranium by Soddy, from polonium by Mme. Curie and Debierne, and from ionium by Boltwood.

It is fitting to recall, before leaving this subject, that Rutherford had previously expressed the idea that the particles "given off by the radioactive elements ought to be made up of atoms of helium."

Another problem, in some degree the reciprocal of the preceding, naturally presented itself: If the disintegration of heavy elements can lead to light elements, would it not be possible, by an inverse method, to condense light atoms into heavy atoms and thus realize in all its fullness the dream of the alchemists? Ramsay was not afraid to take up the subject. Collie and Patterson, having submitted the glass of an ordinary empty tube to cathodic bombardment, had announced the production of helium, which had been formed by the condensation of four atoms of hydrogen. Ramsay confirmed this result, and, going further, found that if the hydrogen is moist—that is, if it is accompanied by oxygen—there will be, moreover, formation of neon, created by the addition of the atom of helium (4) to the atom of oxygen (16). It seemed to him, therefore, that under analogous conditions sulfur would lead to argon and selenium to krypton.

Here, as well, the question should be taken up again. Its breadth, perhaps, surpasses that of all the others. Ramsay will have the honor of having opened up the new field, thanks to his incomparable talent in experimentation, as well as to his boldness and the independence of his scientific conceptions.

These are, in fact, Ramsay's most pronounced characteristics. They are shown again, and in a most brilliant manner, in another work on the radium emanation which he carried out in 1910 with the assistance of Whitlaw Gray. According to the theory of disintegration, the atom of emanation results from the loss of a helium atom by an atom of radium. If the atomic weight of radium is 226 and that of helium 4, the weight of an atom of emanation ought theoretically to be 222. Emanation, whose resistance to all combination had, moreover, been shown, came thus to occupy in the column of rare gases in the periodic system the place predicted for a homolog of xenon. Ramsay wished to prove this by experiment.

And what an experiment! The volume of emanation at his disposal at any one time never exceeded five one-thousandths of a cubic millimeter (much less than the smallest head of a pin), and to determine the atomic weight it was necessary to weigh this infinitesimal volume of gas. A modification of the microbalance of Steel and Grant was constructed, whose sensitiveness attained several millionths of a milligram. The skill shown in preparing, purifying, and weighing the minute quantities of emanation was truly wonderful; and it was this work more than all the others which showed Ramsay's marvelous experimental talent. The result justified the effort. The mean of five determinations gave the number 223 for the atomic weight of radium emanation, a full and complete verification of the theoretical predictions, which Debiere also confirmed by an entirely different method (diffusion).

The brilliance of his work had brought to Ramsay the highest distinctions not only in his own country but all over the world. Academies and learned societies hastened to open their ranks to him. Our Academy of Sciences, which had elected him a correspondent in 1895, named him an associate in 1910. He was also an associate member of our Academy of Medicine. In the year 1904, the Academy of Stockholm awarded him the Nobel prize in chemistry.

One of the characteristic traits of Ramsay's personality was his enthusiasm, which he communicated to all those who worked under his direction, and the impression which he produced on his students, even during a very brief contact, remained ineffaceable. Friendly and patient with all, to "do well," according to his own expression, was all that was necessary to become his friend.

Ramsay was a remarkable teacher with an elegant and picturesque manner of expressing himself, impulsive, clear, concise, and with the great charm of simplicity. In his lessons he did not hesitate at times to use the most advanced teachings; he was the first in England to introduce the works of Raoult, Arrhenius, and van't Hoff.

Everything which lives is in a process of evolution. The real life of an experimental science like chemistry is in progress and

discovery. On this subject, Ramsay was of the opinion that he wanted original research to occupy early as great a place as possible in the work of a student. He distrusted examinations such as are usually held to judge candidates, which were too often dependent on chance. He feared especially that they might result in unjust and unfortunate eliminations capable of discouraging a student in his choice of a vocation. The professor who has followed the student during several years in the course and especially in the laboratory seemed to him to be better fitted than anyone to appreciate his true value. Ramsay always forcefully maintained these ideas and their logical consequences.

In our time of general reorganization, when all institutions and all methods are undergoing revision, it is to be regretted that the great voice of Ramsay is not more listened to in this important matter of teaching.

Ramsay wrote but few didactic works. His little treatise on "Modern Chemistry," which has been translated into French, is a brief but substantial account of the principles of chemical philosophy. The same qualities are found in the highest degree in all Ramsay's writings. They are noted especially in several dissertations in which he developed his own ideas, and whose titles alone are enough to indicate their originality: "The Electron Considered as an Element," "Element and Energy," "Helium in Nature," "Problems Presented by Inorganic Chemistry," etc.

Ramsay was a polyglot and spoke fluently French and German. At the International Congress of Applied Chemistry held in Rome in 1906 he gave in French a lecture on "The Purification of Drain Water," a subject far enough away from the matters of pure science with which he was supposed to be entirely occupied.

From the beginning of hostilities, Ramsay, with his ardent patriotism, threw himself into the conflict. He fought with all the means in his power, through research in the laboratory and through his original suggestions, by pen and word, which he made the auxiliaries of his most indisputable authority. Of him also could be employed the famous phrase, "Je fais la guerre." It was through his persevering efforts chiefly that cotton was, too late perhaps, declared contraband of war. He died in full activity, sixty-three

years old, while his genius was still so rich in promise for science and for humanity, brought down by an incurable disease that carried him off in a few months.

NOTES AND REFERENCES

- 1 Charles Moureu, "Recherches sur les gaz rares des sources thermales; leurs enseignements concernant la radioactivité et la physique du globe," *J. chim. phys.*, 11, no. 1, 63-152 (1913). Charles Moureu and Adolphe Lepape, "Les gaz rares des Grisons," *Ann. chim.*, 9^e s., 4, 5 (1915-1916).
- 2 Charles Moureu and Adolphe Lepape, *loc. cit.*
- 3 "Séparation directe, sans liquéfaction, des gaz les plus volatils de l'air," *Ann. chim. phys.*, 8^e s., 3, 12 (1904).
- 4 Troost and Ouvrard, *Compt. rend.*, 121, 394 (1895); Berthelot, *Compt. rend.*, 120, 581-660, 316 (1895); 124, 113 (1897).
- 5 Charles Moureu and Adolphe Lepape, *loc. cit.*

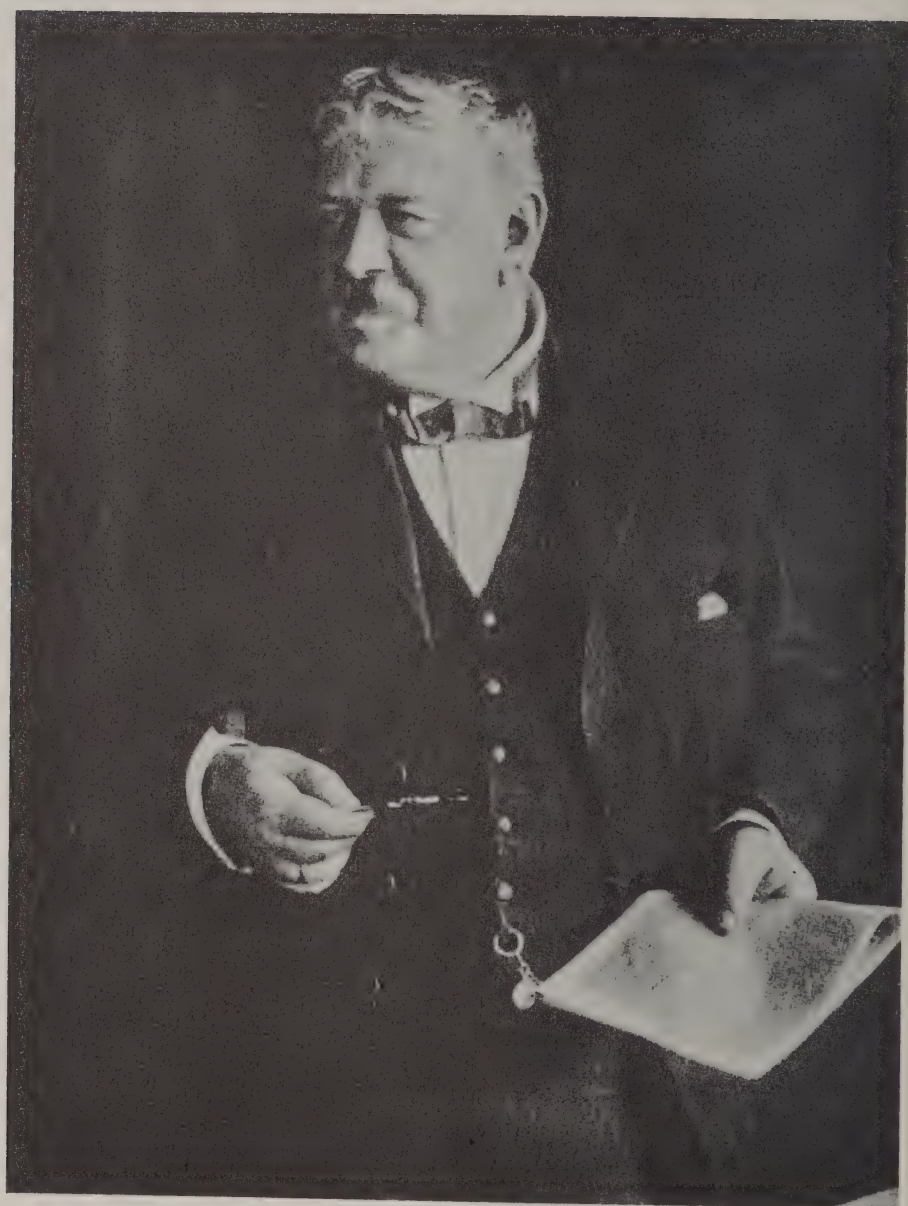
From: *Rev. sci.*, October 1919, in the translation published in Annual Report of the Board of Regents of The Smithsonian Institution, 1919, pp. 531-546, with corrections of translator's errors and some omissions.

CHARLES MOUREU

.. 70 ..

Otto Nikolaus Witt

1853-1932



OTTO NIKOLAUS WITT was born March 31, 1853, in St. Petersburg. At that time, his father, Johannes Niklas Witt, was professor of theoretical and technical chemistry at the Technical State Institution of St. Petersburg (Leningrad). By descent, Otto Witt was three-quarters German, one-quarter Russian. When his family settled in Munich (1864), he went to the gymnasium there. Then he studied at the Zurich Polytechnikum (1871).

A splendid period started in 1870 for the department of chemical technology at the Polytechnikum. Johannes Wislicenus, who had taught at Zurich University, took over the theoretical part and Emile Kopp the technological part of the instruction. Wislicenus left for Würzburg in 1872, but his successor, twenty-six-year-old Viktor Meyer, was his equal.

Emile Kopp had a thorough scientific background and great practical experience in many industries. He had followed the development of synthetic dyestuffs with great interest. To Kopp we owe an elegant method for separating purpurine and alizarine from madder. Dyestuff chemistry was very prominent in lecture and laboratory work. All of us had either prepared, or seen our colleagues prepare, every synthetic dyestuff known at the time, and we were familiar with all the pertinent literature. Thus, when Witt joined the dyestuff plant of Williams, Thomas & Dower in Brentford, near London, in the fall of 1875, he brought with him a thorough knowledge of the field in which he was to work. Only a few months later he produced his two pioneering achievements, the theory concerning the relationship between color and chemical constitution, and the discovery of chrysoidine.

At the dyestuff plant, Witt was charged with scientific work and new developments. Soon he developed the idea that between the practically useless aniline yellow, monoamidoazobenzene, and the technical dyestuff, Manchester brown or Bismarck brown, which is a triamidoazobenzene, there should be a diamidoazobenzene with an intermediate color, that is, an orange. In January

1876 he prepared it by reacting diazobenzene chloride with metapenylenediamine.

Since chrysoidine proved to be of technical value it was put on the market in the spring of 1876, and it was well received by dyers and printers. Up to then only one commercial basic yellow dyestuff, phosphine, had been available, and it was very expensive. Chrysoidine had been obtained a little before Witt by Caro at the Badische Anilin und Soda Fabrik; but the German plant apparently had not recognized its value and began marketing it only after it had become available from England. The method of manufacture was kept a secret. However, early in 1877 A. W. Hofmann published the analysis, the chemical composition, and the method of producing it. It was a good dyestuff for silk and cotton, but less suited to wool which is dyed in an acid bath. Therefore, Witt prepared acidic azo dyes, the tropaeolins.

In January, 1876, Witt published his pioneering paper "Concerning the structure and formation of coloring carbon compounds," which is the foundation of the still dominant theory of chromophores and auxochromes. The only publication on the theory of dyestuffs before 1876 was the famous paper by Graebe and Liebermann "On the connection between molecular constitution and color in organic compounds." This paper is based on Graebe's studies of the quinones and those of Graebe and Liebermann of the anthraquinone dyes and contains the nucleus of the quinone theory of dyestuffs.

Witt formulated three theses: (1) Aromatic compounds become dyestuffs through the simultaneous presence of a color-producing and a salt-forming group in their molecules. The first is given the name *chromophore*; a compound containing a chromophore is not yet colored, in fact in most cases it is colorless and becomes a dyestuff only through the addition of a salt-forming group. (Later on, Witt gave the name auxochromes to the salt-forming groups.) (2) The chromophore exerts its color-producing influence more in the saltlike compounds of the dyestuffs than in their free forms. (3) Of two similar dyestuffs, the one which forms the more stable salts is the better one.

The salt-forming groups, amide and hydroxyl, form parallel

series of dyestuffs with the same chromogen (i.e., the chromophore-carrying substance). Thus, the amide derivatives of azobenzenes correspond to the hydroxyl derivatives, like rosaniline to rosolic acid, etc. He predicted that fluorescein should have a corresponding amide compound; such a compound, rhodamine, was actually found in 1887 by Ceresole.

Witt left England in 1879 and joined the firm of Leopold Cassella & Co. in Frankfurt am Main, working at the *Chemieschule* in Mülhausen. In 1882 the *Verein Chemischer Fabriken* in Mannheim decided to add a dyestuff plant to its other works and offered Witt the scientific and, in part, also the technical direction. Witt accepted and moved to Mannheim. After three years, however, he found out that his field was not industry, but teaching and basic science. In the fall of 1885 he went to Berlin and worked in Liebermann's laboratory. In 1886 he became *Privatdozent* at the *Technische Hochschule* and in 1891 full professor of technical chemistry.

From 1886 on he investigated the peculiar situations arising from the application of patent laws to chemical inventions. The result of this work was a book on "Chemical homology and isomery and their influence on invention in organic chemistry" (1889). This highly interesting book caused the president of the German Patent Office, von Bojanowsky, to invite Witt to give a series of lectures for the members of the Patent Office. These lectures, held in 1891–92, were published under the title "The German chemical industry in its relationship to patent matters."

In 1887 Witt began the publication of a comprehensive technology of fibers, comprising the entire field of fiber production, bleaching, dyeing, and printing.

In 1889, he founded *Prometheus*, the German equivalent to the English magazine *Nature* and the French *La Nature*. He succeeded in obtaining excellent collaborators for his journal, but its main reason of success was the great number of Witt's own literary contributions. The style in which he explained scientific facts and problems to the layman reader of *Prometheus* was a model for every effort in this field.

On March 22, 1915, although suffering from an attack of the

grippe, he went to the session of the Deutsche Chemische Gesellschaft to present his lecture on naphthaline sulfonic acids. That same night, a heart attack ended a life full of work and success.

From: *Ber. deut. chem. Ges.*, 49, 1751-1832 (1916). Translated and abbreviated by Eduard Farber.

EMIL NOELTING

Wilhelm Ostwald

1853-1932



MOST chemists are so deeply concerned with the objective part of their work that they do not reveal much about the life that produced this work. In their autobiographies they will usually tell us more about their teachers and colleagues than about themselves. They are not poets interested in describing emotions and problems of the individual, nor philosophers or psychologists concerned with the general sources of science and thinking.

When Wilhelm Ostwald reached the age of seventy-two, almost twenty years after he had retired from the professorship at the University of Leipzig, he started to write his autobiography.¹ During three years of work, it grew into a 1200-page book and a highly individual story. He was a dexterous and thoughtful chemist, "made from the C-H-N-O-S-P combination from which a Bunsen, Helmholtz, Kirchhoff came . . . an able and very skillful experimenter, mechanic, glass blower . . . an indefatigable worker, clear, concise, strictly logical in oral and literary presentation." Karl Schmidt, his chemistry professor at Dorpat, thus characterized him in a letter of November 8, 1881, written to the director of the Polytechnikum at Riga as recommendation to the post of full professor there. Ostwald also was a philosopher who founded a new journal for the philosophy of science (*Annalen der Naturphilosophie*, 1902) and published several books about it. In addition, he was a psychologist trying to find the general rules of creativity and applying them in a series of books on great men ("Grosse Männer," started 1909). He was also a poet, listening to sudden inspirations, observing and consciously following them. While he freely admitted the existence of the philosopher and psychologist in himself, he would have protested violently against being called a poet. He almost detested poetry although he loved the other arts; he was actively interested in music and painting.

Against being called a poet he would have objected that he observed himself only as he observed any experimental event, and that whenever he generalized from his self-experience he did it as a scientist, not as a poet. Even his activities as an artist, particu-

larly in painting, were mainly introductory, leading to a science of color measurement and color harmonies.

Wilhelm Ostwald was born September 2, 1853, in Riga, the second of three sons. His father had given up the ambition to study art and had followed his father's profession of a cooper. Wilhelm grew up in the joy of making things by hand with the perfection of art as a goal. Whether he made firecrackers or decalcomania picture (by a method he invented for himself), he had no aversion to repeating monotonously the same operation hundreds of times. He remembered, at the time of writing his autobiography, how excited he was when he discovered that there are two places between object and lense where a sharp image is produced, although he soon learned that this had been known long before. He was about fourteen at that time. He was an avid reader, consuming a novel of three volumes in one afternoon.

There are three features of his early youth which remained characteristic and can be recognized in the grown man: persistence in serial experiments, conscious openness to sudden revealing inspirations, and intensity of literary interests. This combination may appear strange; persistence and openness to inspiration, sudden creativity and passive absorption in the work of others seem to contradict each other. However, contradiction is closely related to complementarity and to dynamic balance which, for Wilhelm Ostwald at least, was responsible for much of his work. On the other hand, these three features, or character traits, developed into an inclination to quick generalizations and a certain impatience with people who could or would not follow him. In one of his letters he made a characteristic remark about the inapt quality of people (*die ungeeignete Beschaffenheit der Menschen*) for carrying out his plans. (Letter to Arrhenius, December 12, 1913; see Grete Ostwald: "Mein Vater", p. 164)

As a part of his examinations for the degree of candidate (about equal to a B.A.) he selected to report about the thermochemical work of Julius Thomsen (1826–1909, Copenhagen). "Lightning-like," the thought struck him that instead of measuring heat in chemical reactions, any other property could serve to characterize and follow chemical events in solutions. He was equipped to

measure densities; why not use this easily and accurately measurable property?

With this broad proposition he started on the numerous and repetitive experiments. They led to tables of affinities for 12 acids from 600 measurements of densities and refractive indices. This was his doctor's thesis at the University of Dorpat (1878). He was conscious of having provided not only a considerable number of data, but of having opened a field of investigation that should rank with thermochemistry. The equality had to be expressed in a corresponding name; he selected the term, volume-chemistry.

Since a position at the university was not immediately available, he started teaching at the high school. He did so with such intensity and pleasure that he conceived the need for a textbook. In 1880, the year of his marriage, he found the publisher for it in Leipzig, but the completion took another five years.

In the meantime he became full professor at the University of Riga (1882). For his "studies in chemical dynamics" he constructed an improved thermostat. He measured the rates at which substances like acetamid or methyl acetate were hydrolyzed in dilute solutions containing acids. The "activities" of these acids were the same as those he found in his previous work. The studies by Svante Arrhenius, published in June, 1884, showed him that affinities and electrical conductivity in solution parallel one another. He recognized the originality of his young fellow-chemist and efficiently helped him to find due appreciation. It was as if Wilhelm Ostwald wanted to return in a productive way his thanks for the recognition with which M. M. Pattison Muir (1848-1931, Cambridge, England) had furthered him in 1879. He was happy to exercise this function again a few years later, when he "discovered" the work of Willard Gibbs (1874-78) on thermodynamics and made it available in a German translation (Leipzig, 1892).

Helping others in this way has its rewards. Through Arrhenius' work Ostwald intensified his interest in electrochemistry. For this work he improvised the tools and invented appropriate glass vessels that became standard equipment. In 1884, one result was a "dilution law" for the electrical conductivity of acids in aqueous

solutions, stating that when acid S at dilution v_A has the same conductivity as acid B at dilution v_B , the conductivity will also be the same at the respective dilutions $m \cdot v_A$ and $m \cdot v_B$. This law is actually an approximation; it has to be modified through accounting for interactions between the ions, as was later found.²

The work at the University of Riga was very fruitful, although it also brought some annoying frictions with administrative personnel. Even without such frictions, however, he would have accepted the call to the University of Leipzig. Here, in 1887, he started with two students and a broad program of developing a physical branch in chemistry. The founding of a new journal, the *Zeitschrift für physikalische Chemie* with van't Hoff as coeditor, was only one form for the new program. The title of his textbook expressed it in a different way; it was called "Lehrbuch der allgemeinen Chemie" (1885). Physical chemistry is general chemistry! The great aim was a "chemistry without substances" which he had "always" pursued, that is, "the system of those general concepts and relationships (laws of nature) which can be applied to all substances, without dependence on their nature" (Autobiography, II, p. 387). The last chemical textbook he wrote was called "Principles of Chemistry" and carried the subtitle, "A Chemistry without Substances" (1907).

The year 1887 brought other triumphs of general chemistry in the theory of dissociation by Arrhenius and "the rôle of osmotic pressure in the analogy of solutions with gases" by van't Hoff. Ostwald gave a systematic presentation of this new chemistry in the "Grundriss der allgemeinen Chemie" in 1888 and its importance for analytical chemistry in a textbook in 1893. To understand the new advances better, they should be seen against their historical background. Therefore, he started publishing "The Classics of Science" in 1888. On the other hand, the new technical methods had to be made easily accessible. For this he wrote a physico-chemical methods book (1893). All this occurred while he was engaged in teaching and experimenting and writing papers and book reviews. In one afternoon, he translated a 30 page French publication for the collection of classics in science.

The immersion in all these specific activities still left him time for general thoughts. The most general of these thoughts was con-

cerned with the concept of energy. His early work on chemical reactions aimed at numerical definitions of chemical energy, called "affinity." After a discussion with his students in Leipzig about the problem of matter and energy he perceived the solution in a "lightninglike illumination." It was accompanied by "an almost physical sensation in my brain." Formerly he had been content with a parallelism of matter and energy; now energy became the guiding standard. The mental process culminated in "pentecostal inspiration." It happened while he was visiting a colleague in Berlin, in the spring of 1890. He "recognized that everything we sensually experience can be reduced to energy relationships between our sense organs and the world around us" (Autobiography, II, 158 ff.). On that morning he saw the world—the trees, the birds, the skies—as if for the first time.

Thus he found the key to unlock great treasures of theoretical insight and practical applications. He presented them in a large number of publications in journal articles and books. Their subject surpassed the physical sciences. The biological nature of genius appeared in a new light ("Grosse Männer," Vol. 1: Studien zur Biologie des Genies, 1909). The entire field of culture could now be understood (Die energetischen Grundlagen der Kultursissenschaft, 1910).

A speech he gave at Lübeck in 1895 was greatly misunderstood and violently assailed. The title was: The Defeat of Scientific Materialism ("Die Überwindung des wissenschaftlichen Materialismus"). Before its content became known, he was almost made an honorary doctor in theology as a fighter against materialism; but what he actually said seemed to be worse than even this enemy! Energy as the "final reality" above matter, force, and mind! One special conclusion he derived from his new approach was the abolition of atomism.

After the excitement connected with that meeting in Lübeck he felt completely exhausted. Sleepless nights and inability to work made a long vacation necessary. When he returned to the laboratory in the fall of 1896, he felt his enthusiasm for experimenting gone. He found some consolation in the fact that Liebig had experienced a similar tiredness at about the same age. It is so good to know that when we are weak, we are only normal, subject to an

impersonal rule. And yet, at that time a new institute was being built for him. At the opening ceremonies in 1897, he gave a talk illustrated with experiments on the new liquid air and with a theoretical part on his studies concerning the importance of time in chemical reactions.

Its background was his occupation with the phenomena of catalysis. In 1894, on the occasion of a review in his *Zeitschrift*, he had almost casually formulated a new definition of a catalyst as a substance which influences the velocity of a reaction without taking part in it as a component. He expressed it more succinctly at a conference in Hamburg, 1901: "A catalyst is any substance which changes the velocity of a reaction without appearing in its end product." With all his laboratory weariness he carried out a large amount of experimentation on catalysis.

After unsuccessful attempts to combine nitrogen with hydrogen over in an iron catalyst, he achieved the combustion of ammonia to nitric acid on platinum in 1901. The process was gradually developed to an industrial scale, particularly through the efforts of Eberhard Brauer and the great need for nitric acid during the first World War. In 1917, production of nitric acid by this process reached 26,000 tons (nitrogen equivalent).³

The Nobel Prize in chemistry was given to him for his work on catalysis in 1909. In accepting it, he congratulated the award committee for having selected for the prize that part of his work which he himself valued most highly!

In some respects, however, catalysis was just an incident in his activities. The philosophy of nature occupied a great part of his interests. To the dismay of some philosophy professors, he lectured about it, brought out a book (1901), and founded a journal devoted to this subject. In 1903 and 1904 he was invited to visit and lecture in the United States. In 1905 he was appointed, by the German government, the first exchange professor to this country.

This came just at a time when he was in serious conflict with the University. The particular reason was concerned with religious questions at the official obsequies for Johannes Wislicenus (1835–1902), a freethinker. They came to the breaking point when Ostwald asked to be relieved of lecturing duties. In view of his ap-

pointment as exchange professor, Ostwald accepted the request of the ministry to defer his resignation from the professorship at the University till his return in 1906. Then he was free to devote all his time to his interests outside of university chemistry. He moved to the Landhaus Energie which he built for himself in a suburb of Leipzig.

One of the many things that needed attention was the process of ammonia oxidation. Two patent applications in Germany were rejected because they lacked inventive novelty over previous patents in this field. He became so discouraged that he firmly resolved, after examining his abilities with scientific objectivity, to abandon his efforts in the commercialization of patents and to concentrate on writing books. This occurred in 1907, but he started other business ventures several times in later years, and always with bad results. He wrote a book on the theory of values, but he did not know how to handle the exchange of values in business. This paradox was not the only one in his life. When he described how the universality of energy impressed itself upon him, he deplored that language is apt to mislead; yet he let himself be misled by language when he developed a "mathematical" formula for happiness, and when he uttered other broad generalizations. He relegated historical and artistic work to a level far below science, yet he achieved his best work when he based it on history and art. He dedicated his "Lectures on natural philosophy" (1901) to Ernst Mach, because, among other things, he had declared we must be satisfied with an incomplete picture of the world (*Weltanschauung*) and avoid hypothetical or metaphysical answers to the great questions of life. Neither Mach nor Ostwald had the fortitude—if it could be called fortitude—to live without attempting to answer these questions; perhaps nobody can, except those who are carelessly cynical or emotionally invalid.

Of all his own books, his favorite was one on the history of electrochemistry ("Electrochemie, ihre Geschichte und Lehre, XVI + 1151 pp., Leipzig, 1896"); yet this book was his only one to see not more than one edition.

From the standpoint of his concept of energy he wrote and acted for the organization of science, for a new look on education,

and for a rational foundation of our whole life. He joined in the efforts to create a United States of Europe. Through Ernst Haeckel (1833–1919) he became active in the Monisten Bund. At the end of its congress in Hamburg, 1911, he declared: "Thus I close the First International Monistic Congress and open the Monistic Century!"

Ostwald's sixtieth birthday was celebrated by a great number of his friends, colleagues, and former students in many parts of the world. The Akademische Verlagsgesellschaft in Leipzig (Dr. L. Jolowicz) brought out a privately printed study by Edwin E. Slosson: "Wilhelm Ostwald," as Volume IV of the collection "Grosse Männer," 1913. Slosson added up the literary production of his hero; he counted 22 books (with new editions) containing 15,850 pages, 120 papers with 1,630 pages, reviews of articles on 3,880 pages, book reviews occupying 920 pages, and 300 pages of printed speeches. To this had to be added the volumes of the *Zeitschrift für physikalische Chemie*, the *Annalen der Naturphilosophie*, and 18 of the *Klassiker der Exakten Wissenschaften* which he had edited.

His greatest project for the following years was the theory of colors. It arose out of his artistic interest in painting. Its physico-chemical side had been the subject of his letters to painters (*Malerbriefe*) in 1904. A more academic treatment of the subject followed in 1916. He introduced it with a personal note: "In my psychological complex, there is a strongly emphasized visual element connected with a corresponding memory. As a consequence, color in nature has always excited my liveliest attention and has led to an extended collection of chromatic apperceptions and recollections. The active form of this interest was first carried out in artistic experiments in painting. . . . Another strong element of the same complex, the inclination to form general connecting concepts, had, sooner or later, to result in raising my activity with colors from the primitive artistic level to the higher one of scientific study."⁴

Two historical reminiscences helped him in building a system of colors. One was the psychophysical law which Gustav Theodor Fechner (1801–1887) formulated in 1859: The increase in

magnitude of sensation S is proportional (factor c) to the relative increase in stimulus R :

$$\delta S = c (\delta R/R)$$

The other was the development of photometry in 1760 by Johann Heinrich Lambert (1728–1777). He knew the first from his earlier omnivorous reading, the second because he had included it in a volume of his *Klassiker*. Ostwald rendered previous attempts at developing color scales more definite and precise by adding the scale of "grays" and arranging the colors in a three-dimensional system. In books and charts he published the results of his thoughts and experiments. With the "color organ" he provided a scientific basis for selecting harmonizing values. In this country, his work found active supporters; the Container Corporation of America published a "Color Harmony Manual" in 1942 (with later editions).

In some way, he reverted, on a higher plane, to the kind of activity he had performed in his youth. Just as the boy had patiently filled hundreds of firecrackers, so the septagenarian mixed pigments and printed thousands of strips of paper.

In February of 1929 he presented his new system before the Academy in Berlin. He was proud to find enthusiastic approval from Albert Einstein, but no public agency in Germany could be moved to support his work. His last literary work was a collection on "Goethe, the Prophet" in the year of the one hundredth anniversary of his death.

Wilhelm Ostwald died of uremia on April 4, 1932, survived by the gentle companion of his life, his children, and grandchildren. His daughter Grete converted Landhaus Energie into an Ostwald Museum which persisted through war and Russian occupation.

GENERAL REFERENCES

- J. R. Partington, "Wilhelm Ostwald," *Nature*, 172, 380 (1953).
 Edmund P. Hillpern, "Some personal qualities of Wilhelm Ostwald recalled by a former assistant," *Chymia*, 2, 57–64 (1949).
 Eduard Farber, "A Study in Scientific Genius—Wilhelm Ostwald's Hundredth Anniversary," *J. Chem. Educ.*, 30, 600–604 (1953).

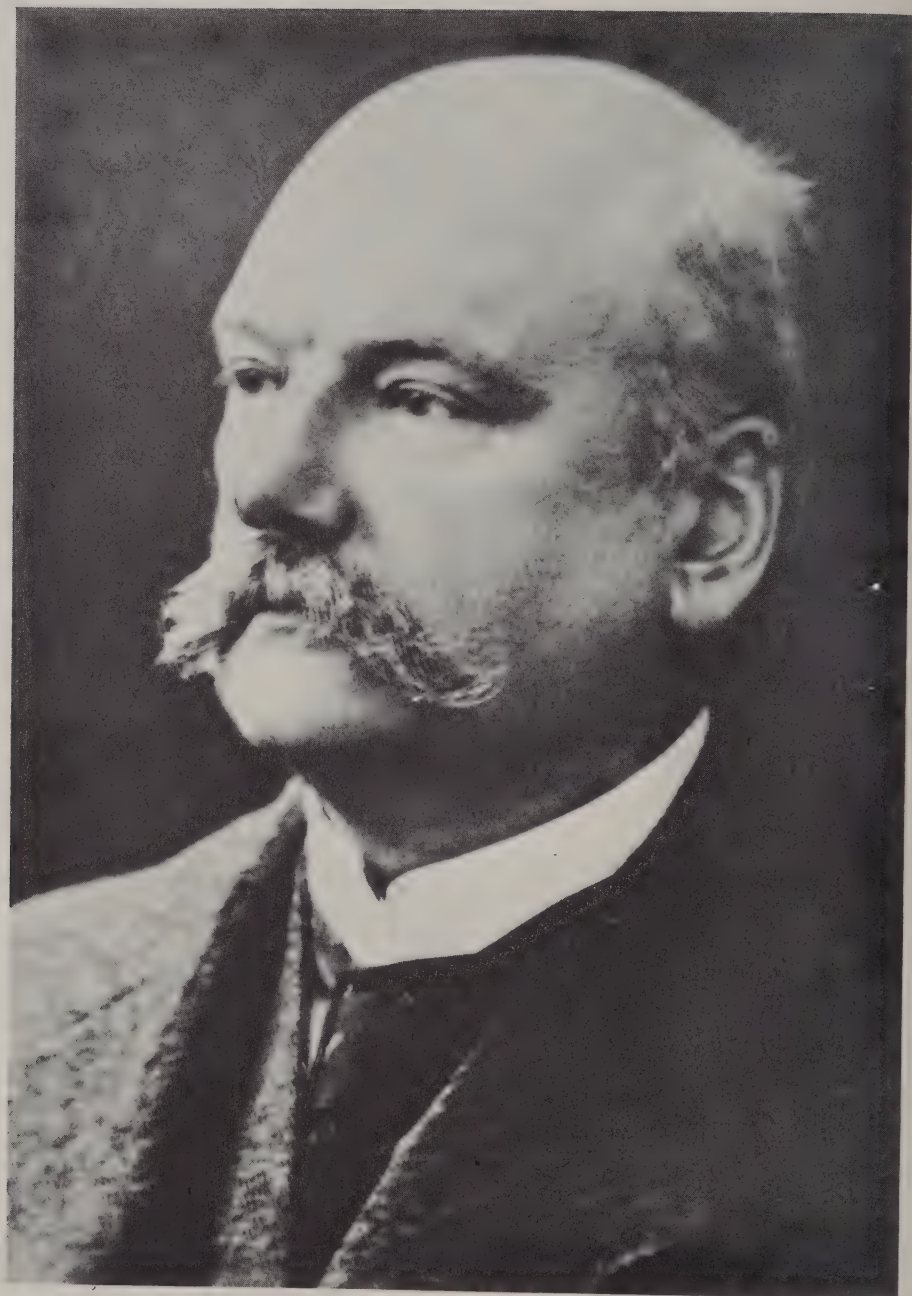
NOTES AND REFERENCES

- 1 This autobiography, "Lebenslinien," and his daughter Grete's book "Wilhelm Ostwald mein Vater," Stuttgart, 1953, are extensively used in the present biography.
- 2 H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, p. 186 ff.
- 3 Alwin Mittasch, "Salpetersäure aus Ammoniak, geschichtliche Entwicklung der Ammoniakoxydation bis 1920," Verlag Chemie, Weinheim, 1953, p. 57.
- 4 Wilhelm Ostwald, "Abhandlungen der Sächsischen Gesellschaft der Wissenschaften," 34, III, Leipzig, 1917; cit. from Grete Ostwald's book, p. 179.

EDUARD FARBER

Albrecht Kossel

1853-1927



ON SEPTEMBER 16, 1953, Albrecht Kossel would have been one hundred years old. Much of what he found and thought for the first time is today such a self-evident part of knowledge that its origin is almost forgotten and scarcely mentioned. Building blocks of proteins, primary and secondary parts of the cell substance, prosthetic groups, and nucleoproteides are concepts that he originated.

Albrecht Kossel was born in Rostock. Although he was at the head of all classes at the Rostock Gymnasium, his inclination was toward physical sciences, not languages. He was especially interested in plants, and he knew their location in the surroundings of Rostock so well that he was entrusted with leading excursions during a meeting of the German Society of Scientists and Physicians. He would have liked best to study botany. However, his father objected for economic reasons. Thus, Albrecht studied medicine, starting in 1872. The newly formed Imperial University at Strasbourg attracted him, and he remained there for almost his entire student time. He spent only a few semesters at Rostock and passed his state examinations there.

At Strasbourg, Felix Hoppe-Seyler (1825–1895) aroused his interest in the new physiological chemistry. Hoppe-Seyler mastered physiology as well as pure chemistry. Albrecht Kossel became his assistant in 1877, and, in 1881, *Privatdozent* for physiological chemistry and hygiene. Two years later, Emil Dubois-Reymond appointed him director of the chemical division at the Physiological Institute at Berlin. This position was not very attractive financially and, because of a heavy teaching schedule, left him very little time for his own research. Nevertheless, he remained there for more than ten years, until he received a call to the Institute of Hygiene at Marburg in 1895. At the same time, the directorship of the Physiological Institute became available to him. Now he was able to unfold his plans freely, and collaborators from the United States, Belgium, England, Finland, France, Italy, Japan, and Russia came to him.

In 1901, he succeeded Willy Kühne (1837–1900) at the Physiological Institute at Heidelberg which he directed until he retired. Heidelberg was the home of his wife, a daughter of the former Germanist Adolf Holtzmann. The International Congress of Physiologists was held at Heidelberg in honor of Kossel. In 1910, he received the Nobel Prize in medicine for "the contributions to the chemistry of the cell through his work on proteins, including the nucleic substances." After his retirement, he worked at the Institute for Protein Chemistry, financed by Fritz Behringer of the firm Oetker's Baking Powder, and with laboratories at the new medical clinic under Ludwig Krehl. There, Kossel worked until he succumbed to a heart attack on July 5, 1927.

Kossel's first publications, in the *Zeitschrift für Physiologische Chemie* founded by Hoppe-Seyler, dealt with a physicochemical theme, the dissociation of salts in aqueous solution by means of diffusion (1878–79). His next subject of research belonged to the field of protein chemistry, the composition of the peptone from fibrin. With his following publication (1879) he entered a field which he was never to leave. He isolated "nuclein" from yeast. At that time, nuclein was the name of an amorphous substance that occurs in all tissues; it contains nitrogen and a high proportion of phosphorus, is soluble in alkalis, and insoluble in water or acids. The first nuclein had been isolated by Friedrich Miescher, in 1869, from the nuclei of pure cells. To Hoppe-Seyler, who knew only lecithin as containing nitrogen together with phosphorus, this discovery seemed so surprising that he delayed publication of Miescher's work for two years. In the meantime, he had checked and completely confirmed Miescher's finding.

The preparation of yeast-nuclein was very simple. Pressed yeast was washed with water, dissolved in alkali, and this solution was added, dropwise, to a hydrochloric acid solution. The precipitate thus formed was nuclein. By boiling with water, Kossel separated this nuclein into 3 fractions: (1) insoluble, free of phosphorus and similar to protein; (2) soluble, containing phosphoric acid as such and in chemical combination; and (3) volatile. The proteinaceous nature of the insoluble fraction (1) was first concluded only from its elementary composition. Later on, the protein was split into tyrosine and several other amino acids. Among the sub-

stances in the soluble fraction (2) were hypoxanthine and xanthine.

This detailed investigation showed that, during hunger, the nuclein-phosphoric acids are much less easily removed from tissues than the other combined phosphoric acids. He concluded that the physiological function of nuclein must be different from that of a reserve substance. It should have a role in the growth of tissues. Thus, the muscle of embryos contains more nuclein than that of the adult animal.

When he analyzed a large quantity of pancreas glands, he discovered adenine which he also obtained from yeast and cell nuclei, from plants, and from the urine of people suffering from leukemia. As a component of nuclein, adenine should occur in all cells that are capable of developing. He found adenine in the alcoholic extract from tea leaves and discovered theophylline on this occasion. In the nucleic acid of yeast he also found an additional component that behaved like a carbohydrate; he thought it was a mixture of a hexose and a pentose.

At this time (1893), Leon Lilienfeld prepared a nucleic acid from the thymus gland. Kossel found that it differs from yeast-nucleic acid and resembles that from sperm. In addition to the previously known cases, he now isolated thymine and cytosine (with A. Neumann).

Thus, Kossel had at hand all the components of nucleic acid, today called deoxyribonucleic acids. Only the carbohydrate had not been identified; Levene succeeded in doing that about thirty years later. Of the components in ribonucleic acid, A. Ascoli, working under his direction, found uracil in 1900; its chemical constitution was established by H. Steudel in 1901.

Kossel described his work on protamines and histones in a monograph which appeared posthumously in 1929. All protamines contain arginine; some have, in addition, histidine or lysine, others again contain all three of the basic substances with a six-membered ring (hexone bases). Of the monoamino acids, alanine and serine are present in all protamines, proline and valine in many of them. In all of them, tryptophan, phenylalanine, and the sulfur-containing amino acids are absent; tyrosine was found only in the protamines of tuna fish and lumpfish (*Cyclopterus lumpus*).

The next step for Kossel was to determine the arrangement of the amino acids in the large molecule of protamines. In connection with these studies, he traced the formation of urea by the action of alkalies on protamines and gelatin.

Kossel once remarked that when he had found a new substance he wanted to continue the work himself on purification, analysis, and chemical constitution. After he had thus identified a specific substance, he started to think about its physiological function. For him, each one of the substances in the living protoplasm was part of a development beginning before this substance's occurrence and continuing afterward. Methods for investigating the intermediary steps in metabolism were not well developed at his time, so that he had to use the chemical structure of a substance as the basis for estimating its origin and future.

In the organs of plants and animals, he always encountered the same group of substances: purine and pyrimidine structures, amino acids, sterols, and others. Obviously, they are fundamental for many processes of life. He called them *Zell-bausteine* (building blocks of the cell) and saw a parallel between them and the basic similarity in histological organization of all cells. From the primary building blocks, he derived secondary ones which differ from one organismic species to the other, sometimes even from one kind of tissue to the other, and are specific for them. Adenine and guanine are among the primary building blocks; theobromine, theophylline, and caffeine belong to the secondary ones.

One of the most important life processes in animals seemed to him the remodeling of the proteins, either by different arrangements of the same building blocks, or by changes within these structural parts. Kossel assumed that during the development of the fertilized egg, the simple protamines and histones are remodeled by a gradual incorporation of monoamino acids. He arrived at this assumption from the fact that arginine (also frequently the other basic amino acids) occurs in all proteins. Often he spoke of the complex proteins as containing a protamine nucleus which could, however, change during the course of growth. Finally, he hoped that a logical systemization of the complex proteins would be achieved if it were possible to find a nucleus of amino acids surrounded by other amino acids in specific arrangements, in

analogy to the benzene ring as a nucleus in many organic compounds. Even if at his time (nor at ours!) a scientifically complete system of the proteins had not been accomplished and a picture of typical proteins could not be formulated, the first steps in this direction had, in his opinion, succeeded in reforming the physiology of nutrition and metabolism.

In his separate papers on his discoveries and observations, Kossel mentioned their general bearing only briefly, if at all. The connections between the special details, and the concepts concerning the chemistry and physiology of protein and the chemical structure of the cell are found only in his general lectures, e.g., in his Nobel Prize lecture (Stockholm, 1910). In an academic speech he delivered as vice-rector of Heidelberg University in November, 1908, he concluded: "The physical and chemical studies of the last few decades have brought us knowledge of phenomena that have completely changed our essential concepts of matter. Newly discovered radiations, the properties of radioactive substances, transformations of the elements—these are processes which provide us with a new theoretical basis for our concepts of the atom. These discoveries have again taught us that we are only beginning to lay the foundation upon which we must build an explanation of the processes of life. We know only fractions of the phenomena to be explained, and we are but starting to develop the means for arriving at explanations. Nevertheless, the hypothesis of vitalism assumes already now that it will never in the future be possible to reduce all the phenomena of life to physical and chemical processes. Regardless of whether this opinion is fully or partially accepted, science will continue to act as if a limit to insight did not exist."

There is scarcely anything fundamentally new that we can add to this standpoint of Kossel's.

Selections from *Naturwissenschaften*, 42, 473 (1955). Translated by Eduard Farber.

KURT FELIX

Paul Ehrlich

1854-1915



BORN at Strehlen near Breslau on March 14, 1854, Paul Ehrlich came from one of those Silesian Jewish families whose members bear a remarkable physical resemblance to each other. They had been scattered all over Germany, preferring academic professions and tending to move in liberal civic circles. Many of them were eminent teachers and some had made reputations in the various sciences. In particular, his cousin Karl Weigert (1845–1904) was a prominent histologist. He was director of the pathological laboratory of the Senckenberg Foundation at Frankfurt-am-Main from 1884 on.

Ehrlich's father was meditative and his mother, in contrast to the mothers of many prominent scientists, was of a decided practical bent.

After the lower school at Strehlen, the boy completed his secondary education at the gymnasium in Breslau. He did especially well in mathematics and Latin. One of the few individual characteristics which can be reported of the reserved youth was exhibited in his treatment of the topic that had been assigned for the compulsory school-leaving essay: "Life, a Dream." The usually cautious Ehrlich boldly wrote that, since life is an oxidation process, dreaming also must be a chemical process occurring in the brain, a kind of cerebral phosphorescence. Quite properly the essay was graded "insufficient," and this mark deprived him of the privilege of being relieved of the oral examination. This penalty was no slight matter to him, and he protested strongly. Obviously, the scientific idea was dominant in him as opposed to the humanistic emphasis which alone was given any nourishment in the Breslau Gymnasium. Like many of the young men of the time he was probably imbued with a Haeckelian philosophy.

Accordingly, he enrolled at the University of Breslau as a passionate realist and had high hopes that the study of science would bring him all that he looked forward to. He followed no special plan in his science courses. He attended the lectures of the great

anatomist Wilhelm Waldeyer who, in grandiose manner, proclaimed the superiority of anatomical concepts in therapeutics. These lectures made a great impression on the young Ehrlich, and it was probably then that he decided to study medicine. He had also regularly heard the lectures on histology by his cousin Karl Weigert. In addition, it is reported that he had avidly read Heubel's book on lead poisoning. Already, Ehrlich had become a peculiar type of medical student, endowed with an excellent ability to learn but interesting himself only in the major and general medical relationships. He attended the lectures of Julius Cohnheim and Rudolf Heidenhain, men who along with Ludwig Traube supported in Germany the other leading ideas of the time, namely, the physiological ideas in medicine and promoted them so effectively that eventually Ehrlich broke away from the predominance of anatomical concepts. At that time already he was envisaging an art of staining microscopic preparations of both healthy and diseased tissues, so well-developed that they could provide direct insight into the life processes. He also was contemplating the world of structural organic chemistry, a branch which was growing to tremendous proportions and, despite its complexity, remained as lucidly and harmoniously beautiful as the many-colored world of microscopic preparations. Moreover, since the dyes, particularly after the preparation of the first aniline dye (mauve) and the synthesis of indigo, had been shown to be carbon compounds with known structures in which the addition and removal of radicals and atoms led to ever-different color effects, pure science and pure medicine were now contiguous in the fields of organic chemistry and histology. In this common area, thought the young student, there would be found the exact scientific medicine that had been the goal of physicians for thousands of years.

It is likely that Paul Ehrlich closed all other books and stopped attending all other lectures. His ability to learn, so definitely exhibited earlier in Strehlen, and shown in his later years over an ever-widening area, was now devoted ardently and exclusively to the study of histology and organic chemistry. After one semester at Breslau he was at the University of Strasbourg for three semesters and then studied at Freiburg and Leipzig. According to

the *vita* submitted with his doctoral dissertation, he took the state medical examination after his tenth and twelfth semesters, a statement that implies that he was obliged to repeat one or more sections of the examination. This autobiographical sketch includes a list of all of his university teachers, and he states that he worked for several years in the laboratory of Cohnheim and Heidenhain. It was there that his first analytical investigations by staining were carried out. During the period up to 1878, i.e., in the course of an unusually prolonged university student career, he evidently had stained countless microscopic preparations and had tested far more than the customary number of dyes before finally submitting his dissertation to the Leipzig faculty. Its title reads: "Contributions to the theory and practice of histological staining". (An English translation, along with the German text, is now readily available in *The Collected Papers of Paul Ehrlich*, compiled and edited by F. Himmelweit, 4 volumes, including a complete bibliography. Pergamon Press, New York, 1957-58.)

This slim composition was lost for many years and was eventually disinterred by Leonor Michaelis, professor of chemical medicine at Berlin. It is assuredly one of the classics in the epoch-making literature of medical science. Even now, its contents have not been exhausted; it affords an incomparable glimpse into the scientific soul of Paul Ehrlich; moreover, it is an excellent key to the subject: "Paul Ehrlich as a Chemist." If no more than his later researches were available, it would be difficult to determine now what his own share had been and how much had been contributed by his co-workers. The dissertation, composed by him alone, tells us what no one can take from Ehrlich; it reveals his unique mentality and proves that, when he left the university and before he was a clinical assistant, he had already embarked on the road that was to make him the founder of chemotherapy. Consequently, this dissertation will be analyzed here in some detail. He himself had discussed this matter in the *Archiv für mikroskopische Anatomie*, 13:263 (1887).

The dissertation is in two parts. The first is headed: "The chemical conception of staining." He proceeds from the fact that despite the tremendous amount of scientific labor expended on the

technique of histological staining, the *theory* of this process had received almost no attention. Hence he begins his scientific investigation by posing an elementary and original question. It is of little import that here too he had had forerunners. It is of significance only that to him the staining in itself appeared to be a fundamental scientific component, superior to all technical details. Even in his early stages he did not limit himself to the specialized literature; he read books on the practice of dyeing and hoped thus to glean basic information extending far beyond the bounds of his particular field. However, he was aware of the limits that would need to be drawn here. For the most part, dyeing is textile dyeing, and at that time this technique was limited to a few materials, principally silk, cotton, and wool. The published information, therefore, derived entirely from the relation of the dyes to these few materials. Moreover, to him it seemed likely than any expected advances would have to come from the territory that is common to the dyers and the histologists. He proved that all selective histological staining, i.e., all staining which is to differentiate between tissues, falls into two large groups. In the first, namely, addition or direct staining, the pigment enters unchanged into one tissue but not into another. In the second category, the so-called adjective staining (dyeing), the coloring matter combines initially with another compound (mordant) such as alum, and then as a color lake adheres to the tissue (fiber). Ehrlich chose carmine to represent the first group of dyes and hematoxylin the second. The simple dye is soluble, the lake is insoluble. He then dealt exclusively with the first group because the majority of histological staining belongs to this category, and especially because the aniline dyes, from fuchsin to eosin, which are so clearly known from the chemical standpoint, belong here. The staining of nerve tissue with gold solutions belongs here also. The question then naturally arises whether the binding of the soluble pigment on a tissue involves physical relations, such as adhesion, or whether there is true chemical union between coloring matter and tissue. It was already known that the animal fibers, silk and wool, are colored by simple bathing in the dye solutions without the intervention of a third material, a mordant. This simple proc-

ess can be translated directly to selective histological stainings. According to Wagner¹ and others, chemical changes do not occur; the animal fibers and the dyestuff remain unchanged. As a proponent of the chemical theory of dyeing Ehrlich first of all selected Schützenberger,² who thought that the animal fibers itself played the part of mordant and through chemical binding deprived the dye of one of its fundamental properties, namely, its solubility; a color lake is thus produced, an organic base takes the place of the usual metal oxide. Ehrlich did not accept the arguments of the mechanists and did not hesitate to combat the seemingly decisive nonequivalence of dyestuff and tissue by citing examples (such as the behavior of mercuric chloride toward silver chloride) to show that pure chemistry also contains instances of compounds which do not conform to the laws of equivalence. When he attempted to carry over into organic chemistry the relationships from inorganic chemistry, he encountered certain difficulties. Inorganic chemistry abounds in double compounds. However, he got around this hurdle by citing little known cases from organic chemistry which can be accounted for by assuming double compound formation, and he thus tried to weaken the arguments opposing chemical binding as the basis of staining.

These speculations by a twenty-three-year-old medical student are rather bold. They might be described as fanciful except for the fact that they constituted the starting point of a road that was to lead straight to those results which converted this medical student into the epoch-making master of the healing art. Perhaps it is not valid to read into those youthful speculations something that properly can only be derived from the eventual successes. However, a remark which occurs at this point in the dissertation shows that, from the start, Ehrlich knew precisely the goal he hoped to reach by means of these "imaginings" to which his predilection for the broader relationships had brought him. In this incidental remark he states:

I have spent somewhat more time on these relationships—which so far as I know, have not yet been expounded—because I believe they have a general medical interest. Thus, those who assume, along with Rossbach, Ranke, Binz, etc.,³ that the alkaloids combine selec-

tively with the protein of the body will feel free to regard elective staining as a parallel to the action of poisons. The difference between them would then reside in the fact that the dyes combine with the dead protein compounds, the alkaloids with the living.

Here is the most fundamental sentence in the dissertation. This far-reaching thought, whose effects were to have a great influence on medicine, was relegated to a mere remark probably because it was included in a doctoral dissertation. At the time of the composition of this essay, any physician who hoped to be taken seriously in science was not permitted to develop any ideas, rather he had to present facts. Therefore, a paper which really should have demonstrated the chemical affinity of specific protoplasmic parts for specific poisons and remedies became instead the doctoral dissertation: "Contributions to the theory and practice of histological staining."

During the rest of his life Ehrlich now had only to develop the idea which he had conceived. He had embarked on a course toward a specific remedy, he had begun with a fruitful method, a method which during his lifetime he found no reason to change. The strength of his work lay in the fact that he had started with selective histological staining and the constitution of the staining agents. Its weakness was the inadequacy of the biology of his youthful years, which while still deeply immersed in an insufficient mechanistic philosophy had no desire to see its own basic problems.

In his dissertation, Ehrlich moreover adopted the views of O. N. Witt, the eminent theorist in the field of dye chemistry, who believed that every aromatic dyestuff must possess a salt-forming group and also a chromophoric group, such as the azo group. In his further exposition, Ehrlich demonstrated that he had a thorough grasp of organic chemistry. He pointed out that all synthetic dyes have either a distinct acidic character, as in the case of eosin, or a marked basic character, such as shown by fuchsin. Instances were cited to prove that it is possible to arrive at desired elective staining on the basis of chemical relationships, and that it is not necessary to rely solely on mere trial and error experiments.

The second and more extensive part of the dissertation gives a description of the chemical, technological, and histological aspects of the aniline dyes. Here once more Ehrlich proves himself to be thoroughly at home in his chosen field; he had become both a genuine medical man and chemist.

Already, at that time, the name Ehrlich was known in German chemical circles and a bright future was foreseen for him. Friedrich von Frerichs (1819–85), director of the medical clinic at the Charité Hospital in Berlin, gave him a position there which he held even after von Frerichs died. In due course he was made senior house physician, titular professor (1884), and in 1887 he qualified as a *Privatdozent*. However, after von Frerichs' death in 1885, Ehrlich's position was not agreeable. The former had looked on him as an exception, had relieved him of routine duties, and had seen to it that he could pursue his researches without interference or annoyance. Things changed when Karl Gerhardt (1833–1902) took over. He did not appreciate the usefulness of a head physician of this type. Gerhardt was strictly a clinician, and it was his aim to train clinical men. Actually, Ehrlich went on as before for a time. In accord with the rules, he was made associate professor in 1890, but his independence of thought and deed carried him more and more out of step with his superior. He had no desire to become a clinician, he wished to remain what he was: a medical research man.

Perhaps it was a fortunate turn of fate that as early as 1887, the sickly young man became definitely tubercular. He applied for leave and, accompanied by his wife,⁴ went to Egypt to recover. He was thus spared the daily wear and tear of the friction with Gerhardt and did not use himself up as has been the case with many of his type. During the years at the Charité he had been extremely active; no less than 44 papers, his book, "Das Sauerstoffbedürfniss des Organismus" (Berlin, 1885), and several doctoral researches conducted under his guidance are the permanent fruits of this period. In contrast to his later practice, Ehrlich had worked almost without collaborators. What help he needed came mostly in the form of expert advice from the chemical industry, with which he had developed close contacts. Because he included

in his researches as many as possible of the aniline dyes that were then being discovered, he required information about their structures and methods of preparation. In turn, he offered useful suggestions to his industrial friends. In particular, von Weinberg⁵ appreciated his talents and gladly provided him with chemicals and useful counsel. Information concerning these friendly contacts is important to the history of chemotherapy. For instance, in his fundamental paper "Chemotherapeutische Trypanosomen Studien" (*Berliner Klinische Wochenschrift*, 1907) Ehrlich wrote:

When I was beginning my experiments, I lacked every outside opportunity to be active in this field of chemistry and, therefore, I am permanently indebted to Arthur von Weinberg for having generously placed at my disposal for many years the rich treasury of his chemical knowledge and talents.

The earliest studies by Ehrlich at the Charité dealt with the staining of white and red blood corpuscles. With the exception of several clinical-anatomical investigations, which may be regarded as *études d'occasion*, these studies of blood cells were his first major pieces of research. After the discovery of leukemia by Rudolf Virchow (1821–1902) and a type of pernicious anemia in 1868 by Anton Biermer (1827–92), a clinical science of blood diseases had been established, and blood preparations had been stained. But Ehrlich was the first to use dyes as reagents to characterize particularly the white corpuscles, and he thus brought order into the confusing multiplicity of forms of these cells under normal and pathological conditions. If he had accomplished nothing beside this, his name would still belong among the foremost clinicians of his time. Entirely apart from the diagnosis of true blood diseases, a methodically stained blood smear is one of the most valuable means of obtaining a picture of the patient's condition not only when he is not suffering from a blood disease in the narrow sense of the term, but when he is ailing in any respect. Thus, Ehrlich's great general principle, at its first application, resulted in an important advance in the field of diagnosis. He might have spent the rest of his life with this lovely method, simple as it was, but he was through with it as soon as he had demonstrated its

great and very important possibilities. He did not become a specialist in blood diseases. Other things were more alluring.

The introduction by Ehrlich (1881) of methylene blue for staining bacteria is most important. All of the dyes previously used for this purpose suffered from the disadvantage that they stained not only bacteria but also, to a greater or lesser degree, tissue constituents, blood corpuscles, serum, fibrin, mucus, etc. Consequently, the bacteria did not stand out distinctly enough. In methylene blue, Ehrlich recognized a dye capable of staining microorganisms and cell nuclei quite distinctly, while coloring the other constituents of a microscopic preparation much less. Among his numerous discoveries, this one marked a decisive advance. At this time, he must have conceived the idea of consciously and planfully constructing a molecule in such manner that it would provide optimum protection to the tissues of the organism and also inflict maximum damage to the microparasite which had invaded the organism. The concepts "organotrope" and "parasitotrope" must have been present in his mind in some form or other at this time. Furthermore, the link with bacteriology had now been found.

The discovery of the diazo reaction in urine (1882) also came during this period. This is still one of the most important reactions for diagnosing infectious diseases. The connection with Ehrlich's stain-analytical studies is obvious. Despite its significance, the discovery of this reaction was not much more than a by-product of Ehrlich's principal researches.

On March 3, 1882, Robert Koch (1843-1910) announced the discovery of the tubercle bacillus to the Berlin Physiological Society. His staining method was cumbersome and yielded poor delineation. The day after this memorable meeting, Ehrlich was able to show Koch the method of staining tubercle bacilli that in essence is still being used. The modern theory of tuberculosis was built up to a large extent by the aid of this method.

In 1885, after Ehrlich had completed the new approach to the blood diseases, he published a fundamental text, "The Oxygen Need of the Organism" a staining-analytical study in which he applied his research principle to the living organism for the first time. What he was now attempting went far beyond the staining

of a microscopic slide preparation; he was dealing with the chemistry of the living cell. He used alizarin blue, a dye that is reduced with difficulty, and indophenol blue, which is readily reduced. He found that certain tissues reduce only indophenol blue, whereas others also reduce alizarin blue. All tissues that reduce the latter also reduce indophenol blue. These processes in the living organism actually involve reductions similar to purely chemical reductions. Nevertheless, Ehrlich recognized a difference. In the living organism, his experiments succeeded, to his amazement, with water-insoluble dyes, whereas, *in vitro*, soluble materials undergo chemical reactions more readily. Living cells cannot be stained by most water-soluble dyes because the coloring matters do not infiltrate these systems. However, the cell is capable of taking up fine particles of certain undissolved dyes and of then converting them into a reactive state. The dyes used must be such that they lose their color when the oxygen is taken from them and regain the color when oxygen is again supplied. Finally, if the dyes are to break down into particles of sufficiently small dimensions, they must form colloidal solutions. In these experiments, Ehrlich also took account of the fact that the dyes are initially taken up on the basis of physical rather than chemical conditions. He prepared coarse-grained, heavy metal lakes and determined what metals are taken up by the various organs. He had reached a point where he could methodically cause a particular metal to be deposited at a designated region in the animal body.

Through these staining experiments it had now become possible to introduce a quantitative aspect into the study of the reactivity of a tissue. It had also become apparent that the affinity of protoplasm for the dyestuff molecules is dependent on whether the protoplasm is dead or alive. At this time he did not yet have available the terminology of colloid chemistry, but it appears he thought that perhaps the physical and the chemical reaction were not so completely separated as the scientists then supposed.

Important fundamental questions remained: What parts of the body or what portions of the tissue are stained when a dyestuff of a particular structure is introduced and then manifests the degree of its avidity for oxygen? How great is this avidity and

how can it be measured? Why are certain portions stained in a particular manner and others in a different manner? Thus the study of the oxygen need of the organism resembled an expedition into rugged virgin country from which the explorer returns and reports merely what he saw, but tells nothing about why he undertook the journey, leaving his audience to guess the reason for the entire venture.

Still another difficulty stemmed from the lack of a general biology resting on proper foundations. When Ehrlich speaks of affinities and avidities, it is not clear whether he is employing these terms in their ordinary chemical sense, or whether he is using them to denote a broader conception of the desire for oxygen in which morphological structure and vitality are factors.

At this stage he had to seek collaborators. Hematology had now come into being with the assistance of A. Lazarus. Ehrlich had associates of marked independent standing. On the other hand, the men who worked with him were placed in his debt because their successes often were in no slight measure due to his brilliance, knowledge, and practical sense. On the whole, it is frequently difficult to assign to his associates all of the credit that may properly belong to them. Ehrlich's researches flowed over into the chemical industry. Institutions as well as individual scientists used his ideas and, in some instances, entered into active association with him.

In the same period that saw the beginning and growth of the staining of living tissues, Ehrlich also discovered the methylene blue staining of the peripheral sensory nerves *in vivo*. About fifteen years later, this finding led to the treatment of neuralgias with this dyestuff, a method which is in line with the methodical administration of remedies of known constitution to act on prescribed tissues. However, the results of vital staining with methylene blue have as yet been far more important as an adjunct to the microscopic anatomical study of the nervous system.

The results of his investigation of thallin, a now-outmoded febrifuge, were published in 1886. This investigation is of importance here, because it demonstrates clearly how far his staining-analytical work of 1878 had already carried him into rational therapy.

These, in brief, were his accomplishments while an assistant at the Charité. On his return, from Egypt, fully recovered, he found the doors of various government research laboratories closed to him for reasons that are now difficult to comprehend. He furnished a small private laboratory in Berlin, disregarding the drain on his limited financial resources, and set to work. He began with the immunization of laboratory animals against abrin and ricin, two virulent poisons obtained from plants. His goal was to show that immunity is a chemical process, and the complete independence of his method of operation is shown in that he did not feel bound by his previous successes. He was now dealing with materials of unknown structure. He was searching for—and found—the only thing that perhaps could be found, the quantitative relation between poison and animal, the basis of the testing methods that had by now become necessary for curative sera. He also worked to discover the hereditary relationships in immunity, and he was also to show that the immune bodies are transmitted to the child by the nursing mother. When Robert Koch brought out tuberculin in 1890, he turned over a clinical observation station in the Moabit Hospital to Ehrlich, and when the Institute for Infectious Diseases was opened, he placed a small laboratory at Ehrlich's disposal. So the years passed, rich in well-anchored work which proved that fundamentally Ehrlich was turning more and more to the immunity sciences.

In the meantime, Friedrich Althoff (1839–1909), the Prussian Minister for Ecclesiastical, Educational, and Medical Affairs, a blunt, odd, but above all intelligent and bold person, had noted that the nation had something exceptional in Ehrlich. But even his influence was not sufficient to induce the Prussian faculties to disregard their ingrained denominational scruples and provide Ehrlich with a position commensurate with his demonstrated abilities. If, in addition to his other handicaps, Ehrlich had now also been entirely deprived of funds, an entire segment of science might have been delayed or even never developed. But Althoff was precisely the man to deal with impossible situations of this kind. If the faculties would not yield, the matter would have to be handled without them. As a result, a Royal Institute for Serum Re-

search and Testing was set up in 1896 at Steglitz, a suburb of Berlin. Two years later, the Institute for Experimental Therapy was founded at Frankfurt-am-Main. This well-furnished laboratory fitted in well with Ehrlich's plans and the mayor's designs for the University of Frankfurt. In 1906 it became still more effective as a research center by attaching to it the Georg-Speyer-Haus für Chemotherapie, built by Franziska Speyer as a memorial to her husband.

Ehrlich proved himself equal to these extraordinary strokes of good fortune. In the years around the turn of the century he evolved the side-chain theory, one of the most controversial scientific postulates of the era. Lauded to the skies by some, declared unworthy of discussion by others, it was also of the highest philosophical interest within the framework of its time. Admittedly it was not entirely what it should have been, but equally it certainly was a fruitful premise for the greatest successes of rational medicine.

The theory proceeds from the simple fact that substances can act on each other only when they are in contact, or to use Ehrlich's own phrase: *Corpora non agunt nisi fixata*. He assumed that every material to which the body reacts fixes itself to the protoplasm molecule of certain cells. This applies to any substance, such as the toxin of an infecting agent, an enzyme, a fat, a carbohydrate, or a protein. He compares the process of infection, which therefore becomes only a special case, with nutrition. In the latter, the ingested foods are assimilated in the protoplasm of the body; in other words, they are fixed in the protoplasm and act then in a sense as the protoplasm of the organism being nourished. Accordingly, the protoplasm molecules must possess many sites for attachment and the material, which attaches itself, must have a binary structure. At its one end, the "haptophoric" group, it must fit into the site of attachment, the "receptor," but it must be able to exhibit its specific action with its free end. In the side chain theory it is assumed that the foreign molecule irritates the cell protoplasm, this irritation consisting in the saturation of the receptors of the cell protoplasm by the haptophoric groups of the foreign material or, in case suitable receptors are not available,

they are produced by the cells initially of their own accord. He called antigens all substances that affect the body in this way, render it immune, for instance. Accordingly, the protoplasm molecule possesses definite places in its receptors for these binary or dipolar antigens, regions or sites that show a degree of similarity to unoccupied chemical valences. These are not true free valences, because the unsaturated protoplasm does not have the character of a nonsaturated chemical compound. In his book on the oxygen need of the organism, and originally also in his theory of the immunizing process, Ehrlich gave the name "side chains" to these sites of attachment. This term quickly acquired a different meaning. According to a rule stated by Weigert, the organism reacts to an injury to any of its parts by overcompensation. Ehrlich assumed that the protoplasm molecule correspondingly reacts to saturation of its receptors by producing an excess of receptors, and that it repels any superfluous receptors and permits them to enter the blood stream. Thus, as a sequel to many infections there are large supplies of free receptor side chains in the blood plasma, where they capture invading infectious antigens; in other words, they attach themselves to the haptophoric groups of the antigen. In the case of diseases which confer lasting immunity, so many free side chains are in the blood that no significant fixations on the cell occur. Consequently, the body can never again fall prey to these diseases and its blood plasma, now a carrier or storehouse of receptors, can serve as a curative serum and also as a protective agent. In this sense the side-chain theory proved of much value; it provided explanations, it revealed relationships, it led to remedies. On the other hand, it has remained a pure hypothesis; a receptor or haptophore group has never been seen.

Ehrlich moved to Frankfurt in 1898 while in the middle of his studies of immunity, while he was engaged in an endless program of researches, and while he had in his hands an apparently inexhaustible method and an extensive supply of modern equipment. Because of his convictions and desires, the new Frankfurt Institut was given the name, *für experimentelle Therapie* rather than *für Serumtherapie*. Evidently he was planning to go beyond serum therapy. Actually, he was destined to take up in Frankfurt

the dyestuff therapy of the protozoal diseases, to advance the treatment of diseases due to spirilli by means of aromatic arsenic compounds, and to arrive at a successful attack on syphilis with salvarsan. Following this triumph, which brought him world-wide acclaim, he was to proceed methodically to the curative action of metalloids and metals, thus laying the foundation for a future approach to the cancer problem.

From 1906, the Georg-Speyer-Haus was also under his direction. The chemical industry in the Frankfurt region provided him generously with compounds, often tailored to fit his demands and suggestions, and these manufacturing establishments also opened their other facilities to him. Associated with him were men who were authorities in their respective fields. Among them were the bacteriologists Max Neisser and Julius Morgenroth; the chemists Robert Kahn and Albert Berthelm, who made notable contributions to the study of aromatic arsenic compounds, Paul Karrer, and Hugo Bauer; Kiyoshi Shiga and Sahaschiro Hata from Japan, H. Apolant, the student of cancer, and others. These men, some as employees, others as members of the staffs of the two institutes, had under them sections of the various fields of the investigations on which Ehrlich was working concurrently, or in the course of time they had charge of sections in which they continued to work independently after Ehrlich had turned to other topics.

Ehrlich was at the peak of his career in these Frankfurt years. From his little room, where he was almost buried under heaps of journals and other papers, lines of communication ran to the scientific centers of the whole world and to the expeditions investigating places of epidemics. Almost all of the honors and recognitions than can come to a scientist were conferred on him. In 1907 he was made Geheimer Obermedizinalrat, and in 1911 he became Wirklicher Geheimer Rat with the title Excellency. The Nobel Prize in Medicine and Physiology was divided between him and Elie Metchnikoff (1845–1916). His life from 1902 to 1915 and his special working habits are charmingly pictured in "Paul Ehrlich," written by his secretary, Martha Marquardt.⁶

Ehrlich designated as "amboceptor" every side chain, hence every receptor, which is so constructed that one of its ends can

g. d. D. a. u.
d. d. d. u.

1) Wäre es interessant zu sehen ob
 $\text{Ph} \text{---} \text{CH}_2 \text{---} \text{N}(\text{H}) \text{---} \text{CH}_2 \text{---} \text{N}(\text{H}) \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{Ph}$
 sich beim Selenieren
 verhält. Tetramethyldiamido-selenopyren.
 Ich würde sehen, ob man
 nicht ausgangsmaterial
 herstellt.

2) Wie die Telluro-pyrenie
 hätte ich schon angestrebt

3) Guckte ob man das Neben-
 thio-pyren noch verwenden
 könnte leicht erhalten kann!

4) ~~Wie~~ Die Analyse wird
 wohl zeigen, ob das ~~früher~~
 beschrieben ~~thio~~-selenopyren
 noch ~~ausgangsmaterial~~ ~~hergestellt~~
 werden kann.

dunkel, wie die dimethyldiamido-selenopyren.

One of the program notes, written by Paul Ehrlich to Dr. Hugo Bauer, dated May 17, 1914. It starts out: "1. Would it be interesting to see how (2,2' diamino-4,4' dimethyl-diamino-diphenyl-methane) reacts with selenium? Tetramethyldiamido-selenopyrene? I shall see whether one can get starting material." The other paragraphs refer to the corresponding compounds with tellurium and with sulfur ("thio-").

anchor the antigen, for instance, a bacterium, a toxin, etc., while its other end carries groups of atoms which can combine with atom groups taken up from the blood plasma, so that they bear on this other end the so-called complement, the supplementary portion. This, again, is initially no more than a symbolic picture to illustrate the fact that the immune bodies, etc., are active only when they are bound to fresh blood serum, no matter (to a certain degree) whether the serum comes from the same animal as the antibody or from another animal. While the amboceptors themselves are strictly specific, the complements are nonspecific. The theory of complements was then further developed and led to ideas which proved to be very important. Jules Bordet, bacteriologist and pathologist, director of the Pasteur Institute at Brussels, who received the Nobel Prize in 1919, and Gengout had prepared their hemolytic system from red corpuscles and sera which dissolved red blood corpuscles. With the aid of these combinations they had worked out a serodiagnostic method for many pathogens. August von Wassermann (1866–1925) director of the department of experimental therapy at the Koch Institut for Infectious Diseases, from 1906 director of the section of experimental therapy and biochemistry at the Kaiser Wilhelm Institut in Berlin-Dahlemin, following in part the imaginative scheme evolved by Ehrlich, made the capital discovery (1908) that syphilis in man can be detected by the complement-fixation method. Further investigation disclosed the astounding fact that the Wassermann reaction actually does not disclose the presence of antitoxins combating the spirochetes but, instead, shows the presence of an entirely different body, probably a lipoid-like degradation product of the body cells that have been damaged by the spirochetes. In this case, a false lead resulted in a very important discovery. It becomes quite evident here that what Ehrlich had pursued from his staining-analytical experiments on was not real chemistry; instead he had developed a symbolic description of a natural process, i.e., a fictional approach quite in the sense of the Hans Vaihinger's "As If" philosophy. (Compare, in this connection, Robert Koch's "Das Als-Ob im ärztlichen Denken," Munich, 1924.)

Ehrlich had the ability to close his interest in a field of study

that had not been exhausted. The studies within the frame of the side-chain theory were continued until 1904. He then began his work on the experimental treatment of cancer, which occupied him until 1906. These researches, conducted in close association with H. Apolant, produced only a number of observations and insights into spontaneous and induced cancer in laboratory mice.

Ehrlich now embarked on his final and most excellent field of study. This was no less than an attack on protozoal diseases and spirilloses by chemical agents, whose structures were known and could be systematically modified. The first trials were made with dyestuffs, then came the aromatic arsenicals. He had accordingly returned to the methods of his earlier years; he had reverted, at least with respect to the curative agent, to purely chemical methods. Now, under the most favorable external circumstances, his great talent and wealth of knowledge and ability could once again be applied to this important field. With the aid of the side-chain theory he had already arrived at a procedure which, as Weigert early appreciated, had its weaknesses. Even though it had yielded many facts, this line of attack had not been able to demonstrate that blood contained immune bodies as a secretion which could be isolated and chemically explored. Particularly in his letters to Weigert, Ehrlich revealed how he was occasionally disturbed by the inadequacy of the basic biological ideas on which the symbolically designated concepts were supposed to rest. However, something entirely different came to be involved. Ehrlich had realized that the potentialities of the purely biological experimental therapy were exhausted for the time being. It must have been gratifying that he could revive the idea of internal disinfection, thus becoming the father of chemotherapy, with which he was destined to surpass the treatments based on experimental therapy, that is, the therapy with curative sera and vaccines.

His goal had now become to find materials that would inflict as much damage as possible on the pathogenic agent without appreciable damage to the afflicted organism. To use his terminology, this meant the use of curative agents that combine the highest parasitotropism with the lowest organotropism. He wished, so he stated in one of his favored comparisons, to shoot magic bullets

which would strike only the invader, not the victim. He coined the expression, embodying the desire of which he may have already dreamed in his early years, "*therapia magna sterilans*," the specific healing by means of a remedy which, once administered, destroys the causative agent root and branch. This magniloquent expression, which did not entirely live up to its promise, reveals the romanticism that tinged Ehrlich's precise studies throughout his career.

It is not surprising that Ehrlich began with trypan red, since the use of dyestuffs had been the subjects of his earliest researches. Trypan red with one stroke actually did cure mice that had been infected with trypanosomes. It surely was a great moment when, for the first time, he saw mice survive a deadly dose of these organisms, and when peering into his microscope he found that the blood no longer contained trypanosomes. Trypan red is an azo dyestuff and Ehrlich believed the curative action resided in the azo group $N=N$. It was an obvious step to go from nitrogen to related elements, and it was not long before he was making analogous trials with arsenic compounds. It was found that all strains of trypanosomal organisms are destroyed by arsenic compounds, but that certain strains become resistant to arsenic after several transfers from host to host and repeated exposure to arsenic. This finding of course gave rise to explanatory theories.

His studies with arsenic compounds led Ehrlich to investigate atoxyl, which Paul Uhlenhuth, professor of hygiene and bacteriology at Freiburg, had used (1905) to combat fowl spirillooses and which even then had been pointed out by the latter as being effective against syphilis. Although not the first, Uhlenhuth had discovered the curative action of arsenic compounds against protozoal diseases. Charles Laveran and Mesnil had found already in 1902 that arsenious acid is active against such diseases in laboratory mice. Actually, a rather old remedy was being applied here, because prior to the introduction of cinchona bark (1638) arsenic was used, though with trepidation, against malaria, which is a protozoal disease. In 1905, Koch also used atoxyl in the treatment of African sleeping sickness, but with unsatisfactory results.

In the short span of a human lifetime, Ehrlich had acquired a

masterful ability to manipulate molecules almost at will and by planned alterations of the molecules to arrive at compounds possessing carefully calculated curative effects. His letters, notations, and other memoranda show clearly the chartered course of his researches. Those who think that he merely used a cut-and-try method when testing the host of compounds that came to him from many sources are in error. Of course the valuable aid given to him by the chemical industry and by his own chemical associates must not be forgotten—assistance which he gratefully welcomed. Soon after atoxyl had come on the market (1902) Ehrlich and Shiga tried its action on trypanosomes, but the particular strain, the only one available to them, did not respond. In 1905 he again turned his attention to this compound and together with Berthelm found that atoxyl is the monosodium salt of paraaminophenylarsinic acid, a crystallizable compound.

This finding opened the way to chemotherapy employing aromatic compounds of arsenic. The next hurdle to be surmounted was an adequate method for preparing sufficient quantities of this "arsanilic acid" or its sodium salt. Ludwig Benda, a chemist at the Cassella Company, accepted this assignment and worked out the procedure in the plant laboratory. Ehrlich's demands on the chemists often reached incredible heights, and it was only because of the efficient collaboration of experienced and inventive chemists like Benda that his desires were met to some extent.

However, atoxyl could not be regarded as a final solution to the problem of treating human patients suffering from diseases due to protozoa or spirilli. It was too toxic and left undesirable after-effects, particularly disturbances of vision. The monosodium salt of an acetyl derivative or arsanilic acid, acetarsanilic acid, was widely used under the name "arsacetin." It was much less toxic than atoxyl, but it also left disturbances of vision as soon as the amount administered reached the point at which a cure could be expected with a single dose.

Atoxyl and also arsacetin killed the parasites *in vivo* but not *in vitro*. Recalling his experiences on the oxygen need of the organism, he now tried previously reduced aromatic arsenic compounds. About this time, Benda on his own initiative prepared

parahydroxymetanitrophenylarsinic acid and sent it to the staff at the Speyer-Haus for reduction and testing. Through an error the compound was not used. Knowing nothing of this older specimen, Ehrlich and Bertheim prepared this compound some time later and reduced it. The reduced product (*p,p'*-dihydroxy-*m,m'*-diaminoarsenobenzene) later was named Salvarsan. In the meantime Albert Neisser had carried out his transmittal of spirochetes to anthropoid apes and to rabbit testes and had successfully treated this inoculated syphilis with arsenic preparations. Moreover, Hata, who was familiar with the technique of transmitting syphilis to rabbits, came to the Georg-Speyer-Haus early in 1909. Now the chief objects of attack in the chemotherapeutic researches were the spirilli of relapsing fever and the spirochetes of syphilis in place of the trypanosomes. A preparation bearing the laboratory number 606 was superior to all others with respect to rabbit syphilis. It was the hydrochloride of the reduced product just discussed, namely, salvarsan.

A patent covering the "Ehrlich-Hata 606" was applied for in 1909. Ehrlich put the preparation into the hands of several trusted physicians. The first favorable results were announced in 1910 at the Internists' Congress held at Wiesbaden. Slowly and cautiously Ehrlich widened the circle of physicians entrusted to use "606." They numbered around 500 by the time salvarsan was placed on sale in the apothecary shops. The method of administration was quickly improved. In neosalvarsan (arsphenamine) whose effective constituent is the sodium salt of dihydroxydiaminoarsenobenzene monomethane sulfinic acid, the physician had available an agent that could be injected intravenously, and in this form it largely superseded salvarsan. Eventually, other salvarsan compounds made their appearance, including myosalvarsan, which can be injected subcutaneously, and spirocid which is easily taken by mouth. The complex silver salts of salvarsan and neosalvarsan were found to be very effective.

No medicinal preparation had ever been so thoroughly studied as salvarsan. Because of it, syphilis became better understood and the medical treatment of this scourge became more fundamental than before. The success of salvarsan was one of the great events

in medical history, and following in Ehrlich's footsteps, other valuable chemotherapeutic agents appeared. Pertinent instances are Optochine which is a specific against pneumococci, and Germanine which is useful against sleeping sickness. The fact that salvarsan and its derivatives have now been displaced by antibiotics and sulfa drugs takes nothing away from their usefulness and merit at the time they were in use.

World-wide acclaim came to Ehrlich, especially at the International Medical Congress at London in 1913. A *Festschrift* was issued on his sixtieth birthday on March 14, 1913.

The outbreak of World War I proved fatal to Ehrlich. To him it signaled the collapse of his ideal: the peaceful competition of all peoples in humanitarian endeavors. Seriously afflicted with arteriosclerosis, his health deteriorated rapidly. He died on August 20, 1915, and was buried in Frankfurt-am-Main.

GENERAL REFERENCES

- Paul Ehrlich Centennial, New York Academy of Science, Annals, vol. 59, Art. 2, pp. 141-276, 1954.
 Paul Karrer: Paul Ehrlich, J. Chem. Education, vol. 35, pp. 392 / 6, 1958.

NOTES AND REFERENCES

- 1 J. Rudolf v. Wagner (1822-1880), professor of chemical technology at Würzburg. For many years he was the editor of the *Jahresbericht über die Fortschritte* (later *Leistungen*) *der chemischen Technologie*.
- 2 Paul Schützenberger (1829-99), professor at the Gewerbeschule in Mülheim, then in Strasbourg and from 1870 in Paris.
- 3 Michael J. Rossbach (1842-1894), medical doctor and pharmacologist at Jena. Heinrich Ranke (1830-1909), pediatrician and professor at Munich. Arthur H. Binz, professor and director of the Chemical Institute of the Landwirtschaftlichen Hochschule (Agricultural College) in Berlin was head of the chemical section of the *Speyer Haus* in Frankfurt from 1918-21. He also served as chief editor of the *Zeitschrift für angewandte Chemie*.
- 4 He married Hedwig Pinkus in 1883, when she was only nineteen.
- 5 Arthur von Weinberg (1860-1943), chemist and, from 1883, director of Leopold Cassella & Co., and then a member of the board of the I.G. Farbenindustrie.

PAUL EHRLICH

- 6 Martha Marquardt, "Paul Ehrlich als Mensch und Arbeiter," Deutsche Verlagsgesellschaft, Stuttgart, 1924. An extended English edition of this book, with the title, "Paul Ehrlich," with an introduction by Sir Henry Dale, was published by Henry Schuman, New York, 1951.

Selected from Bugge, *Das Buch der Grossen Chemiker*, 2, 421-442.

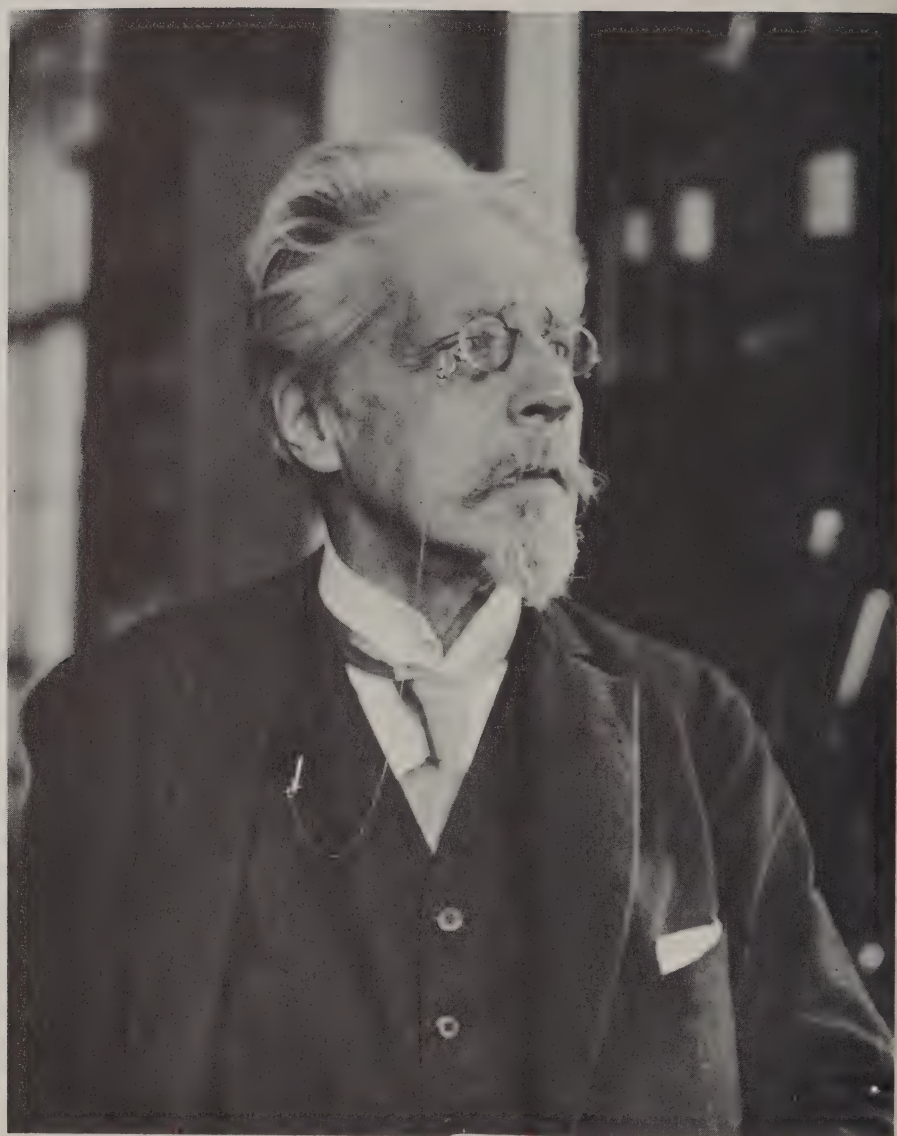
Translated by Ralph E. Oesper.

RICHARD KOCH

.. 74 ..

Arthur Rudolf Hantzsch

1857-1935



ARTHUR RUDOLF HANTZSCH¹ was born in Dresden on March 7, 1857, a year notable to chemists by Kekulé's publication on the constitution of mercuric fulminate in which he enunciated the tetravalency of carbon. The town of Dresden, situated where the Elbe River leaves the mountains, is beautiful not only because of its location but also because of its buildings and art collections. Augustus the Strong had built a palace in elegant baroque; here was the seat of a brilliant opera and of one of the great collections of paintings. These surroundings may well have influenced Hantzsch, who even as an old man possessed and admired elegance of bearing, of language, and of taste. Hantzsch's father was a wholesale dealer in wine, carrying on a business which had been founded by his grandfather, originally a cooper. His mother was the daughter of an artist, Prof. J. U. Bähr, of Riga. According to his own account, Hantzsch was an emotional child with little self-reliance. He had many interests and developed early a love for nature and the sciences dealing with it.

Animals and particularly the records of their prehistoric forms fascinated him. It is not likely that these subjects were treated to any considerable extent in the curriculum of the famous Kreuz Gymnasium which he attended, but the adolescent was also gifted for languages and enjoyed the sound of spoken Greek so much that he studied this language privately. A flair for language, for communication by the written and the spoken word, confidence that words can transmit complicated thoughts and intuitions, and annoyance when communication failed were characteristic of Hantzsch in later years.

Chemistry was not taught at the Gymnasium, but Hantzsch must have had some contact with it from quite an early age. He has recorded that chemistry, which had seemed mysterious, gradually replaced zoology as his main interest, and that he carried out some chemical experiments while he was attending the Gymnasium. Subjects in which he was not interested were neglected, and Hantzsch left the Gymnasium in 1875 with only a moderate cer-

tificate. Such records are not infrequent in the lives of great scientists and make one wonder about talent lost by too rigorous elimination at the college threshold.

As soon as Hantzsch had obtained his matriculation certificate in 1875, he began to study chemistry under Professor R. Schmitt and Dr. W. Hempel at the Polytechnikum (now the Technische Hochschule) in Dresden. Schmitt, a pupil and later an assistant of Kolbe, was a man of great ability, known for working out a large-scale process for the production of salicylic acid by Kolbe's reaction, and for his discovery that phenolsodium carbonate is an intermediate in this synthesis. He was one of those who, led by Hofmann, had in 1867 founded the German Chemical Society. Hantzsch received the greater part of his formal scientific training under Schmitt and his colleagues. It culminated in a thesis "On Paraoxyphenetol and Some Aldehydes and Alcohols Derived from Hydroquinone" which Hantzsch submitted to the faculty of the University at Würzburg in 1880. He had worked in Würzburg for one semester, completing the thesis because the Polytechnikum in Dresden was not entitled to grant a doctor's degree. The professor of chemistry at Würzburg was Johannes Wislicenus. Thirteen years later Hantzsch became his indirect successor in Würzburg, and he succeeded Wislicenus at Leipzig in 1903. Wislicenus must have examined Hantzsch in chemistry. The other subjects of the doctor examination, passed *summa cum laude*, were physics and mineralogy. One of Hantzsch's contemporaries in Würzburg remembers him as an extremely hard worker, mixing little with fellow students, and, apart from his research work, much preoccupied with his engagement—dating from 1879—to the eldest daughter of the sculptor Johannes Schilling, whom she had served as model for the figure of Germania in the Niederwald monument on the banks of the Rhine. This monument and the reports of contemporaries testify to her great beauty. While in Dresden, Hantzsch had served a year in the Army.

The young doctor spent the summer of 1880 in Hofmann's laboratory in Berlin working on a few, not very exciting organic problems. For the beginning of the winter semester, Hantzsch accepted a position as instructor in the Institute for Physical Chemistry of the University at Leipzig under Gustav Wiedemann.

Hantzsch, however, devoted his experiments to a synthetic problem in organic chemistry, whose brilliant solution established the fame of the 25 year old as the originator of a new synthesis of the pyridine nucleus. Baeyer had obtained collidine (sym-trimethylpyridine) by heating acetaldehyde ammonia. Stimulated by this work, Hantzsch examined first the behavior of ketones with acetaldehyde ammonia and obtained at high temperatures a mixture of pyridine bases which could not be resolved even by repeated fractional distillations. Then Hantzsch tried the reaction of acetaldehyde ammonia with ethyl acetoacetate. One mole of the aldehyde ammonia with two moles of the keto ester lost three moles of water in a smooth reaction, and the diethyl ester of dihydrocollidine dicarboxylic acid was obtained. Oxidation, saponification, and decarboxylation led to the free sym-collidine formulated in Hantzsch's "Habilitationsschrift" as the symmetrical trimethylpyridine in analogy to benzene. On the cover of this thesis, Hantzsch issued an invitation to his "Probevorlesung" (trial lecture) on "The Relation between Chemical Constitution and Physical Properties of Organic Compounds." This lecture represented the last of the obligations which Hantzsch had to fulfill in order to obtain the *venia legendi*, i.e., the right to lecture at the University as a "Privatdozent." This coveted right is bestowed by a German faculty only after close scrutiny of the candidate, after he has shown by his Habilitationsschrift the ability to carry out independent research, after a colloquium at which any member of the faculty may question the candidate and after the Probevorlesung.

The contents of the Habilitationsschrift were published in a paper in Liebig's *Annalen* in 1882. Work on the syntheses with α -keto esters and aldehyde ammonia compounds and on the chemistry of the reaction products occupied Hantzsch for the next three to four years. He stayed in Leipzig until 1885. He had married in 1883, and we can assume that the young, successful Privatdozent with his beautiful wife was happy in the town famous not only for its University, but for its Gewandhaus orchestra, for its Conservatory of Music, as the seat of the Supreme Court, as the center of German book printing and publishing, and as an important commercial center. Kolbe ruled over chemistry at the Chemical Insti-

tute of the University. As editor he used the *Journal für Praktische Chemie* to review and criticize, often scathingly, the happenings on the chemical scene. He had suggested that Hantzsch publish the collidine synthesis in his Journal. When Hantzsch refused, the temperamental Kolbe told Hantzsch, "Then we are divorced people." Nevertheless Kolbe prophesied that he would one day be his successor in the Leipzig chair.

Kolbe was also one of those who recommended Hantzsch as his second choice when the head of the Swiss school authorities, the able Kappeler, consulted him about a successor for Victor Meyer who had left the Swiss Federal Institute of Technology to accept a call to Göttingen. Kolbe's first choice was Ernst von Meyer, his son-in-law. There were others who had recommended Hantzsch as their second choice, but like Kolbe's, their first choice had been influenced by personal reasons. Sitting unannounced in the audience among the students, Kappeler listened to Hantzsch and decided to offer the twenty-eight year old Privatdozent the full professorship in Zürich. This was in the Zürich tradition; Victor Meyer had been twenty-four years of age when he was called to this chair. There was free exchange of academic personnel between Germany and Switzerland, not even a change in nationality was required. Hantzsch had entered the exalted group about which—as the story goes—the archangels had once complained to the Lord; these men enjoyed greatest independence, highest social position and income, and longest vacations, and all that for following their heart's desire. The Lord had replied that there was justice, though hidden, because He had created their colleagues.

Hantzsch spent eight fortunate and happy years in Zürich. His two daughters and one son were born there. In the Swiss mountains he found both aesthetic and physical satisfaction, and the freedom of religious and political opinion in Switzerland was in accord with his own liberal outlook. Throughout his life, and not least at the end, the Swiss Federation was for him the pattern of a fine national and social organization. He called Switzerland his second Fatherland, and few of his vacations in later life were spent elsewhere. He worked, and worked his collaborators hard in the laboratory, but on weekends and during vacations he and his assistants joined in strenuous and courageous hikes and mountain

climbs. Roland Scholl told of these excursions when he came to Leipzig to celebrate Hantzsch's seventieth birthday.

Although Hantzsch never abandoned synthetic work, his chief interest was not the preparation of compounds, but the relationship between physical and chemical properties and constitution, the subject of his Probevorlesung in 1882. Synthesis to him was a tool rather than an end. The proper interpretation of experiments in which Tscherniac had obtained the first synthetic derivatives of thiazole led to a thorough investigation of these compounds, stimulated by Hantzsch's interest in chemical "mimicry." This term, adopted from zoology, was used for compounds which "simulate" the behavior of other chemical individuals. Thus, thiophene had been found by Victor Meyer to resemble benzene, although it contains one sulfur atom instead of an ethylene group. Similarly, thiazole resembles pyridine from which it differs by replacement of ethylene by sulfur.

There are four major topics which dominated Hantzsch's interest, oximes and the stereoisomerism on $C=N$ bonds, diazo and azo compounds and the stereoisomerism on $N=N$ bonds, the relationship between physical properties (particularly light absorption), and structure, including the intricacies of the sterical arrangement of atoms in molecules and the nature of acids and bases. The interest in stereochemistry was marked by the publication, with his pupil Alfred Werner, of a paper on stereochemically isomeric compounds of nitrogen. Johannes Wislicenus had shown that compounds with carbon to carbon double bonds can form cis- and trans-isomers depending on the orientation of the substituents on the doubly linked carbon atoms. In the paper which opens the 1890 volume of *Berichte der Deutschen Chemischen Gesellschaft*, Hantzsch and Werner extended this interpretation to compounds with carbon-nitrogen double bonds and explained the super-numerary isomers which had been observed with oximes and other compounds containing carbon-nitrogen double bonds. At the end of this paper, Hantzsch gave Werner credit for having independently "formulated the central idea with its most important consequences, when I first expressed the vague idea that nitrogen, just as well as carbon, might give rise to geometrical isomerism." While Werner's share in the formulation of the new theory is

great, the experimental proof was due wholly to Hantzsch's energy and experimental skill. In one year, working with substances which were frequently extremely labile, he accumulated with his collaborators evidence for the stereoisomerism, and for the tautomerism, of the oximes.

With methods similar in principle to those used by Wislicenus he sought to decide for the aldoximes which of the respective compounds were the *cis*- and which were the *trans*-isomers. Likewise, the Beckmann arrangement was used not only to obtain a new line of evidence for the structural identity of isomeric ketoximes, but to establish their "geometrical" configurations. The basis of these correlations was the assumption that intramolecular reactions of groups prove their proximity not only in ring closures but also in elimination reactions. This principle was widely accepted until Meisenheimer proved in 1921 that the Beckmann rearrangement proceeds as a *trans*-reaction. Wislicenus, and after him Hantzsch, formulated their correlations on the basis of mechanical analogies. At that time the quantum theory had not yet made investigators cautious in the use of mechanical analogies for phenomena at molecular dimensions.

Many of the leading chemists of Hantzsch's generation, particularly the organic chemists, devoted a considerable part of their labors to compounds of biological, medicinal, or technical importance. Their contributions, therefore, can be appreciated not only by the progress which they made in isolation, analysis and synthesis, and in the understanding of the reactions of compounds, but also for the significance of these compounds in biology, medicine, and industry. Hantzsch's interest was elicited by the chemical problem as such. The relation of chemical and physical behavior to structure as represented by formulas and models dominated his work. While he rejected concern with practical applications of chemistry, he was tireless in his quest for knowledge, determined, skillful, and inventive, and interested in inorganic as well as organic chemistry. He was guided in the choice of his research by observations which indicated problems the elucidation of which would lead to a better understanding of chemical systems and their transformations. He had an extraordinary ability to see analogies and correlations between seemingly unrelated properties.

His interests were wide, but he was always occupied and pre-occupied with chemistry. In talking to his collaborators he referred to little notes, often jotted down at night, and they might receive postcards and letters written on vacations with questions, suggestions and ideas.

In 1893, Hantzsch published in Zürich a small volume, "Grundriss der Stereochemie."² In the same year, having declined invitations to chairs in Kiel, Worcester, Mass., and Rostock, Hantzsch left Zürich to succeed Emil Fischer at Würzburg. Fischer had admired the synthetic work of the young Hantzsch, particularly his collidine synthesis, and had recommended him as his successor. In Würzburg Hantzsch spent what he remembered as the happiest and most carefree period of his life. He liked the small town, the easy and stimulating social intercourse of all ranks in the University from professors to students, and the beautiful surroundings which invited excursions. His first task in Würzburg as it had also been in Zürich, was to supervise the erection of the new laboratory. It had been planned by his predecessor, but some minor changes were made to increase the accommodation for physicochemical work. Among the men with whom Hantzsch associated in Würzburg was Wilhelm Röntgen; the two families were close neighbors.

During the early years at Würzburg, Hantzsch completed the work on geometrical isomers on carbon-nitrogen bonds. In 1894 he published his first paper on the diazo compounds in which a similar isomerism was proposed for nitrogen to nitrogen double bonds. This led into the chemistry of diazo and azo compounds. With consummate experimental skill in preparative work and by the application of physicochemical measurements, particularly cryoscopic determinations and conductivity measurements, he elucidated the maze of inter-relations between the diazonium compounds containing quaternary nitrogen, the geometrical isomers of diazo compounds with trivalent nitrogen, and the reactions of these, often unstable, substances.

The geometrical isomerism on $C=N$ and on $N=N$ double bonds was not universally accepted. Victor Meyer and Karl Auwers did not trust the formulation of *cis*- and *trans*-oximes, and even the discovery of isomeric hydrazones did not convince them in the beginning. A controversy arose which was noteworthy for the

courtesy displayed by both sides. The work on diazo and azo compounds became the subject of more acrimonious debate with Ludwig Bamberger, Hantzsch's successor in Zürich. After many years of argument, this controversy ended with the acceptance of Hantzsch's point of view by Bamberger in 1912. In later years, Hantzsch referred with regret to the sharpness of this debate; he was greatly affected by Bamberger's long illness and spoke of him with great warmth of feeling and sympathy. Such feelings might also come to the surface impulsively and unexpectedly in his relations with the members of his laboratory, particularly his collaborators and the staff. Hantzsch, though reserved, was not wont to disguise his judgments of criticism or of appreciation and his frank statements could, on occasion, greatly enliven discussions after lectures and at faculty meetings.

While Hantzsch used chemical symbols and formulas, not only as a means for recording results and as an aid in constructive thinking, he was aware of their limitations. He realized early that the more reactive form of tautomeric compounds—compounds in which two or more forms are in rapid exchange—might channel a reaction so that only derivatives of this species are isolated, even though the parent form be present in the starting material as trace amounts only. Hantzsch writes:

It must become more generally recognized that we cannot explain chemical reactions by structural formulae, for by them one can represent only the initial and the final state of a system. And even the possibility of this will become the smaller, the further we depart from the chemistry of carbon, in which the theory of valency founded wholly on structure has proved so valuable, and go over into the chemistry of other elements.

Moore states about Hantzsch's work on diazo compounds that he "widened the experimental basis of his research in every possible direction, seeking in each class of substances for its most stable member, and since he was convinced on general grounds that tautomerism played a great part in the reactions, allowed for this in the choice of experimental conditions and in the interpretation of his results. Gradually he built up a technique which, on the or-

ganic side alone, is a marvel of insight and ingenuity. Even more important historically is the decisive part played for the first time in this research by physical methods of investigating organic problems." While Hantzsch had great imagination and insight in applying physical data to chemical problems, he preferred to leave the tedium of measurements and mathematical details to his collaborators.

The work on the diazo compounds became the backbone of a book, "Die Diazoverbindungen" published in 1902, and republished with many additions by Hantzsch and Reddelien in 1921.

The changes in constitution of acids or bases in the formation of salts had been important in the work on diazo compounds. Such changes became the object of special investigations in which Hantzsch showed that aliphatic nitro compounds form salts not in the nitro form but in a tautomeric aci-form. As a result of this work Hantzsch published in 1899 a paper dealing with the characteristics of salt formation involving constitutional change. It was postulated that such a change can reveal itself in several ways; by abnormal and time dependent neutralization and hydrolysis phenomena and by changes of color in salt formation and in the liberation of acids and bases from salts. In some cases constitutional changes may suppress certain reactions, e.g., with phosphorous pentachloride, phenylisocyanate, and dry ammonia, while the compounds nevertheless give salts. The formulation of these postulates marked a milestone in the understanding of anomalous salt formation. Not all the postulates stood the scrutiny of later experiments and interpretations. In Hinshelwood's³ description of the development of a theory, Hantzsch's paper may be classified as the first stage of "oversimplification, reflecting partly the need for practical working rules, and even more a too enthusiastic aspiration after elegance of form. In the second stage the symmetry of the hypothetical systems is distorted and the neatness marred as recalcitrant facts increasingly rebel against conformity. In the third stage, if and when this is attained, a new order emerges."

Hantzsch owed his call to Würzburg mainly to the brilliant synthesis which he had discovered; the call to Leipzig as the successor to Wislicenus which he received in 1903 must have been

prompted by his accomplishments as a physical organic chemist. Thus, we find Hantzsch in Kolbe's chair 21 years after Kolbe's prediction. He occupied this chair for a quarter century until his retirement in 1927.

The chemical laboratory in Leipzig was located in a large rambling building on the Liebigstrasse, a few minutes' walk from the Laboratory for Applied Chemistry and less than a mile from the Laboratory for Physical Chemistry, where Wilhelm Ostwald taught. The residence of the director was connected to the building; it had ample rooms and a little garden, much used by Hantzsch and his family during the summer months. The big auditorium accommodated about 350 students. There was a laboratory bench for demonstrations, large blackboards stretched along the wall in the rear of the bench, and covering hoods which were also accessible from an anteroom containing all sorts of facilities for the preparation of demonstrations and a collection of chemicals. Hantzsch lectured five times a week from 9:15 to 10:00 in the morning, during the summer semester on inorganic chemistry, during the winter on organic chemistry. As head of the department, Hantzsch gave the "Grosse Vorlesung" (big lecture), as was customary in German Universities, which was attended by beginners not only in chemistry but also in medicine, physics, and general science, and a grand lecture it was. The assistant, an experienced mechanic, had spent much of the preceding day under Hantzsch's direction setting up series of experiments which were run off while Hantzsch lectured from a few notes jotted down on a little card which he carried in his vest pocket. The lecture was brilliant; the delivery reflected Hantzsch's keen interest in the subject; and formulas and equations were developed on the blackboards in his clear handwriting. The blackboards were flanked by two doors leading to the preparation room and crowned by marble busts of Kolbe and of Wislicenus. In celebration of Hantzsch's 70th birthday in 1927, his pupils had a large bronze relief of Hantzsch made which was installed in the center over the blackboards.

After the lecture, Hantzsch used to make the round of his graduate students, discussing with each of them the problems at hand and often doing small-scale experiments—watchglasses

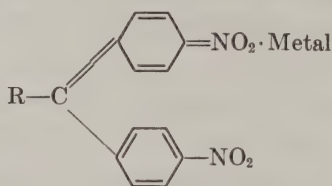
were his favorites when he observed color changes or tried to make recalcitrant substances crystallize. A similar visit took place in the afternoon. As an examiner Hantzsch was more interested in the students' ability to think in dealing with chemical problems than in their cramming knowledge. He was impatient with slow wit, apt to blame it on drinking, and he did not disguise that the habits of German fraternities, particularly their duelling, were not to his taste. The staff of the laboratory included a number of faculty members who taught in various fields of chemistry, and with their assistants and pupils were engaged in research; K. Schäfer and F. Hein in inorganic chemistry. H. Stobbe, G. Reddelien and C. Weygand in organic chemistry, and B. Rassow in chemical technology.

Shortly after his return to Leipzig, Hantzsch's wife died. He remained a widower for seven years and then married Hedwig Steiner of Zürich. The later years were clouded by the tragic death of his only son, who having served as a very young man in World War I, was killed in 1921 on the Grossglockner in the Alps in an attempt to rescue other climbers who were in danger. The tragedy for Hantzsch was accentuated by the death during the same year of one of his sons-in-laws, Professor Löhlein, who succumbed to an infection which he had incurred performing an autopsy. Outwardly he reacted to these blows by working even more intensively with his students and at his desk.

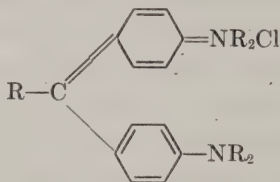
Hantzsch continued in Leipzig the research initiated at Zürich and at Würzburg, but more and more his interest centered around the relations between color and constitution. The guiding concept of this work was that profound changes in color indicate changes in structure which can be represented by structural or stereochemical formulas. Solvation without change in chemical structure of the solute could produce only minor shifts in absorption. Conversely, minor chemical changes like the replacement of a hydrogen atom by a methyl group would as such have little or no effect on light absorption, unless the location of the methyl group differed from that of the hydrogen.

In the investigations centering around the relation of light absorption to constitution, Hantzsch encountered the limitations of classical structural symbolism. He made use of the insight

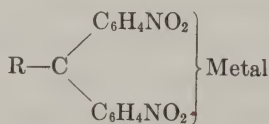
gained by Werner that metals which are bound in the classical way by replacing ionizable hydrogen can, in addition, form intramolecular complexes and cause the formation and variation of colored salts in systems like the violurates. The chemistry of organic metal complexes led Hantzsch to the conclusion that absorption phenomena can be explained by the assumption of intermediary states which we would now call resonance hybrids. Hantzsch realized that the stable state of certain molecules would have to be described as an intermediate of more than one structure. About the salts of dinitro-triphenyl methane



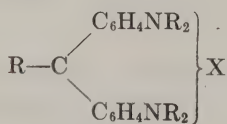
and of di-amino-triphenyl methane



with bases or with acids, respectively, he wrote: "The difference between the quinonoid and the nonquinonoid part of the conjugated complex does not really exist, for in every other way there is identity. The formulas can be simplified to



and



He realized clearly that the difference between the quinonoid and the benzenoid part of these molecules has vanished and that the respective moieties are intermediate in character between benzenoid and quinonoid.

Similar considerations were applied to acids. In this work, the publication of which began in 1917 with a paper on the ultraviolet absorption of carboxylic acids and their salts and esters, Hantzsch tried to penetrate into the nature of the acidic function and its dependence on chemical structure. He showed that acids in aqueous solution are present more or less as hydronium salts, $X^-[H_3O]^+$, which he formulated like the oxonium salts of Baeyer and Villiger and Collie and Tickle in analogy to ammonium salts. He realized that the hydrogen ion of the Arrhenius-Ostwald theory is, in fact, the hydronium ion, and that in aqueous solutions the acidic functions attributed to the hydrogen ion are those of the hydronium ion.

Carboxylic acids form the hydronium salts $RC\overset{\bar{O}}{\underset{O}{\parallel}}\bigg\}H_3O^+$ in which

the two oxygen atoms of the carboxylic group are equivalent. The extent of hydronium salt formation of these acids depends on the concentration of H_2O and on the nature of R , i.e., on the content of real, ϵ -acid, form— $RC\overset{O}{\underset{O}{\parallel}}H$ —and of ester, ψ -acid, form—

$RC\begin{matrix} \nearrow OH \\ \searrow H \end{matrix}$ —in the undiluted acid. Similar ϵ and ψ forms contribute

to the structures of other acids, including the mineral acids. Inasmuch as the ψ form does not exhibit acidic functions, these functions are developed when weak acids are diluted with water. The acidic function of strong acids, however, in which the ϵ form predominates, is diminished by aqueous dilution because *the tendency to form salts, the essence and the real measure of acidity*, is partly used up in the hydronium salt formation.

In discussing acids at the Centenary of the *Gesellschaft Deutscher Naturforscher und Aerzte* at Leipzig in 1922, Hantzsch talked of certain carboxylic acids, as 70% in the ϵ and 30% in the ψ form. There was consternation and Kurt Hans Meyer came to Hantzsch's assistance by interpreting the data as a kinetic equilibrium between both forms, but Hantzsch agitatedly insisted that each individual molecule was to be represented by 30% of the one

and 70% of the other form—years before the theory of resonance was formulated. With oxygen-containing solvents like alcohols, ketones or ethers the acids may similarly form onium salts, or such solvents may stabilize the non-acidic ψ -forms of the acids. A principal means for detecting acidic functions and strengths of acids were basic indicators which, competing with the solvents for the acids, form more or less of the indicator salts and by their color indicate the position of the equilibrium involving acid, solvent and indicator. Another means for measuring the strength of acids was the rate of decomposition of ethyl diazo acetate which depends on the degree to which the diazonium salt is formed. When these ideas were applied to strong acids and measurements of the rate of inversion of sucrose were included, the now well accepted sequence of strength of the mineral acids, perchloric, hydrobromic, hydrochloric, nitric was established.

It is noteworthy that Brönsted, in his classical paper on *Acid and Basic Catalysis* states, "we may find after all—in spite of much divergency—that the ideas of Hantzsch are, in many ways, not incompatible with those of the present review."

Hantzsch used physical properties not only to characterize stable forms but also to gain evidence concerning entities which could not be isolated but are present, for example, in solutions in absolute sulfuric acid. The insight thus gained led to some of the most brilliant experiments in Hantzsch's career, the formation of salts by mixing nitric acid and perchloric acid or acetic acid and perchloric acid and their characterization by conductivity and incompatibility with those of the present view."¹¹

It was Hantzsch's genius to use widely different methods to gain information about a system. Optical data of absorption and refraction, conductivity, catalytic and direct chemical action, and other methods served in unison to elucidate the problem at hand. The physicochemical data, however, were often not obtained with the most perfect quantitative methods. It was the concerted interpretation of these data together with information about behavior in reactions, with other chemical data, and with analogies which yielded results of often amazing perspicacity. This method was attacked by specialists who had obtained measurements of higher accuracy and who objected to the far-flung conclusions Hantzsch

drew from "semi-quantitative" data. Hantzsch felt hurt by the insinuation of carelessness and frustrated by misunderstanding. When, however, a colleague offered a more profound, a more mathematical or a more general approach, Hantzsch was delighted and generous in his acknowledgement.

When Hammett, in 1926, published his first paper on the theory of acidity Hantzsch wrote him expressing his interest and pleasure:⁴ "That you unconditionally acknowledge my theory of acids and were even able to give its mathematical foundation pleases me particularly because most of the German chemists and particularly the physicochemists ignore or even refuse it."

Many honors came to Hantzsch; he received titles and honorary degrees, became a member of several academies and an honorary member of the Chemical Society, but few scientists of his stature have been criticized with the aggression to which he was exposed. Part of this is due to the fact that he reinterpreted the results of others, which naturally caused irritation. Part of it was caused by Hantzsch's method of roaming all over chemistry and chemical physics in collecting data and drawing analogies. In addition, his use of symbols could cause misunderstanding. The operation of any symbol reaches cases where the symbol no longer adequately represents the observations. The mathematical symbol is then modified by further approximations. Structural symbols may be redefined by additional qualities, e.g., statements about size may supplement elements of location. Hantzsch's stereochemical concepts and ideas on the specificity of affinities, for instance that sodium is preferentially linked to oxygen but that silver may be bonded to nitrogen are cases in point. The difference between homopolar (covalent) bonds and heteropolar (ionic) bonds which Hantzsch suggested was not readily accepted. Hantzsch's understanding sometimes transcended the correlations which could be logically deduced from the data, and his assistants were sometimes amazed by the conclusions at which he arrived intuitively from seemingly unrelated observations. Hantzsch's eagerness to understand old and to discover new facts was that of the great scientist. He would have agreed with William Herschel's statement, "If we add observation to observation, without attempting to draw not only certain conclusions, but also conjectural views from them,

we offend against the very end for which observations ought to be made."⁶ With his ability to recognize analogies and to suggest interpretations, Hantzsch combined a keen ability for observation. He told the writer that it was not important which chemical problem he tackled as long as he followed up courageously those of his observations which he could not understand and did not pause to rejoice in verifications of his predictions. "What one can predict is not new anyhow." Verification of prediction interested him only where the experiment confirmed or contradicted a theory. Since Hantzsch wrote to Hammett, the approach to chemical problems has greatly changed and Hantzsch is now widely recognized as a pioneer in the application of physical methods to chemical, and particularly organic chemical, problems. What many of his contemporaries called speculation has become the fountainhead of important developments in physical organic chemistry.

Hantzsch's 70th birthday, in 1927, was marked by a celebration attended by representatives of universities and scientific societies, by colleagues and former students. Many had come to Leipzig, others had written or wired; F. Bergius, K. H. Meyer, T. S. Moore, R. Scholl, F. Hein, K. H. Bauer, G. Reddelien, H. Hibbert, C. Weygand, F. Timm, A. Weissberger, H. Carlsohn, and A. Burawoy were among his pupils the nor later in academic positions; a great number attained distinguished careers in industry. Hantzsch, who was a reserved man and in general rather adverse to display of emotion, was deeply touched—particularly by the respect and affection demonstrated by his former students.

Shortly after his 70th birthday Hantzsch retired from his official duties. He continued work on his publications and he maintained several assistants, selected from his most gifted recent pupils, to continue experimental work on various problems. As his retirement approached, Hantzsch, maybe for the first time in his life, had also accepted the offer of an industrial firm to supervise some of their research. A special small laboratory was installed in the basement of the laboratory building, and there, in great seclusion, he proceeded with work probably on vulcanization catalysts for rubber; the smell of thio compounds and Hantzsch's interest in thiazole and other sulfur chemistry led to this interpretation for the mysterious happenings "in the cellar."

When, about a year after Hantzsch's 70th birthday, his second wife died, he moved to Dresden, to a house in the neighborhood of the Gymnasium he had attended as a boy. No longer responsible for a large laboratory and deprived of the companionship of his wife, he became even more occupied with his research. He paid frequent visits to Leipzig to supervise the work of his assistants. Work and the happy association with his daughters, grandchildren, and a few intimate friends occupied his remaining years. His reaction to the Nazi government was shame and deep disgust, and he went out of his way to express these sentiments in calling on Jewish colleagues. His mind and body remained vigorous up to the time of his death in 1935 at the age of 78.

GENERAL REFERENCES

- A. Burawoy, "Arthur Hantzsch," *Ber. deut. chem. Ges.*, 68, 65 (1935).
- B. Helferich, "Nachruf auf Arthur Hantzsch," *Ber. Math.-phys. Kl. sächs. Akad. Wiss. Leipzig*, 87, 213 (1935).
- T. S. Moore, "The Hantzsch Memorial Lecture," *J. Chem. Soc.*, 1936, 1051.
- Fr. Hein, "Arthur Hantzsch," *Ber. deut. chem. Ges.*, 74, 147 (1941).

NOTES AND REFERENCES

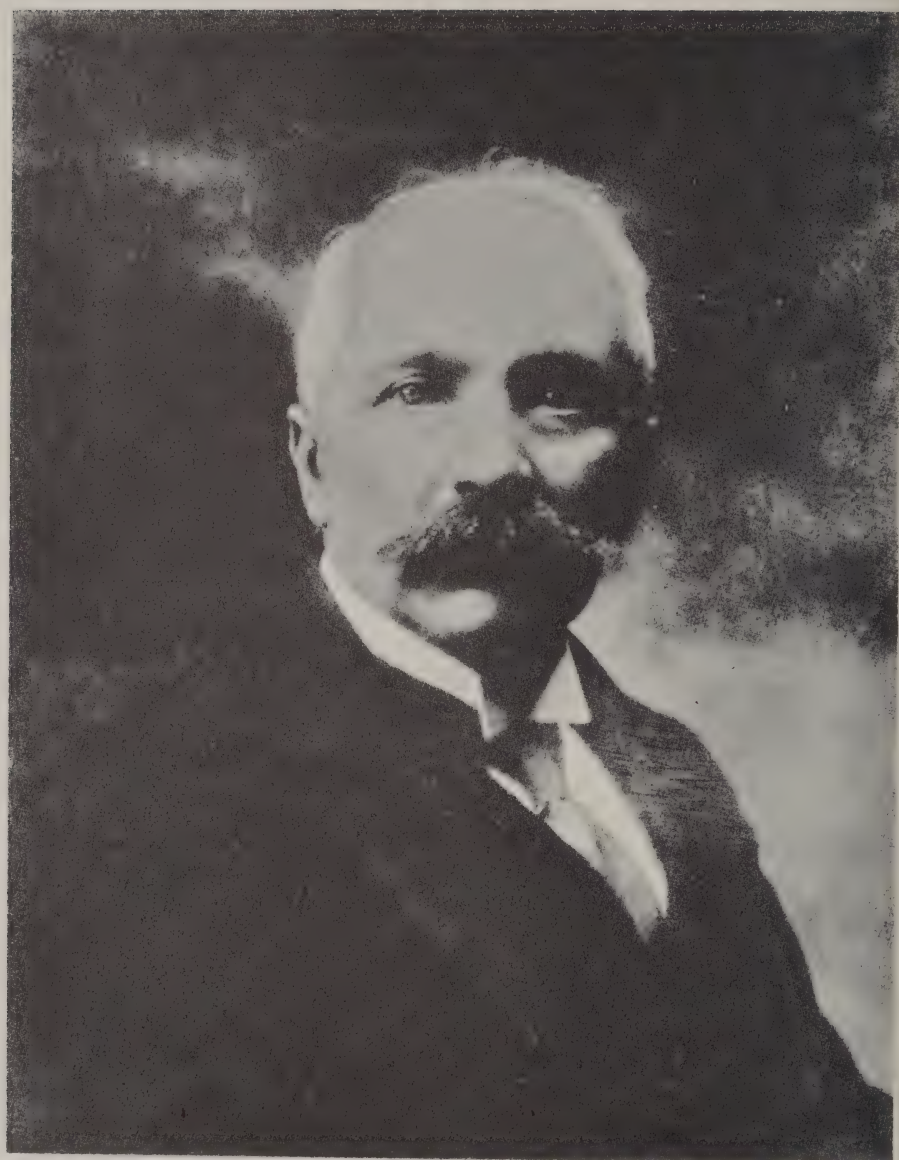
- 1 This biographical sketch leans heavily on T. S. Moore's Hantzsch Memorial Lecture, *J. Chem. Soc.*, 1936, 1051, from which passages are quoted verbatim. In this lecture Professor Moore, a pupil of Hantzsch during the Würzburg time, discusses Hantzsch's work with full use of chemical symbols. The indebtedness of the present writer to Professor Moore and to the authorities of the Chemical Society as copyright owners is gratefully acknowledged.
- 2 Second edition, Leipzig, 1904.
- 3 C. N. Hinshelwood, *Chem. & Ind.*, 1957, 1642.
- 4 I am grateful to Professor Louis P. Hammett for permission to quote from this letter.
- 5 Quoted from Milton K. Munitz, "Theories of the Universe," Glencoe, Ill., p. 264.
- 6 *Chem. Rev.*, 5, 337 (1928).

ARNOLD WEISSBERGER

.. 75 ..

Giacomo Ciamician

1857-1922



GIACOMO LUIGI CIAMICIAN was born in Trieste to a family of Armenian origin on August 25, 1857. He first studied in his native town where Auguste Vierthaler was his chemistry professor. Later, at the University of Vienna, he studied with Barth and Weidel. After having applied himself to natural science, he decided definitely for chemistry, but he certainly would not have been successful in his experiments in plant chemistry if it had not been for his profound knowledge of botany which he had acquired as a young student.

In 1880, he passed his examinations for his Ph.D. at the University of Giessen and then went to Rome, attracted by the reputation of Stanislao Cannizzaro, who made him his assistant at the Institute of General Chemistry of the University of Rome. He stayed seven years at the laboratory of this illustrious master. During this time he continued his beautiful researches on pyrrole and its compounds, which he had started in Vienna; he obtained brilliant results that assured his reputation in all scientific circles.

In 1887, he became professor of general chemistry at the University of Padua; in 1889, he applied for, and obtained, the correspondent chair at the University of Bologna. There he lectured until the last days of his life, teaching with equal success general and inorganic chemistry as well as organic and biological chemistry.

Ciamician was not only a very competent laboratory man and an indefatigable worker, but he also was a teacher of the first order, who was able to communicate to his students his love for physics and chemistry. In 1908, before the Société Chimique de France, he gave a well-received account of his work on photochemistry, which made his audience appreciative of his talents as a speaker as well as of the originality and the interesting subject matter of his researches.

Giacomo Ciamician left us important scientific contributions; although most of his publications appeared in the Italian periodicals, he often honored our *Bulletin* with memoranda of remarkable

clearness. The work of Ciamician is chiefly connected with physics, organic chemistry, photochemistry, and plant chemistry; it was pursued without relaxation from 1877 to 1922, and was only interrupted by the premature death of the illustrious chemist.

At the beginning of his scientific career Ciamician was interested in spectroscopy; he made a comparative study of the spectrum of homologous elements belonging to the same group in the periodic system. His researches in this field were those of a forerunner, because at the present time we recognize the value which it is possible to attribute to the spectographic techniques in theoretical chemistry as well as in many analytical applications.

The research which Ciamician dedicated to organic chemistry was mostly connected with the chemistry of pyrrole and its derivatives. Its close affinity with chlorophyll and hematine are well known, and one finds it again in the nucleus of numerous alkaloids. His investigations in this field were undertaken from 1880 to 1888 and have been described in nearly 80 memoranda. The monograph which he published in 1888 on "pyrrol and its derivatives" won a prize from the Academia dei Lincei. In 1904, he published the general results which he had obtained in the *Berichte* of the German Chemical Society. In the course of these researches Ciamician prepared the tetraiodopyrrol or iodol, which constitutes an interesting successor of iodoform.

During ten years, from 1889 to 1899, Ciamician studied the essential oils of numerous plants: parsley, celery, anise, sassafras, clove, etc. Particularly known is his work on the transformations of saffron and eugenol into their isomers, very important reactions in the heliotropine and vanillin industries.

His research on photochemical reactions was the subject of more than 50 notes published from 1900 to 1915. They form a very important and very original part of the work of this scholar. We all are aware of the considerable upswing in photochemistry since this epoch, and particularly the work of Daniel Berthelot, our eminent late colleague, is present in our memories.

In 1886, in Rome, Ciamician had described the effect of light on nitrobenzene in an alcoholic solution; he returned to this question and studied it systematically in 1900. On June 6, 1908, he explained his work on photochemistry at a conference of the So-

ciété Chimique de France. He had been led to this study by the idea that, in biology, using only the means Nature has at its disposal, it is indispensable to reproduce all the substances composing organized beings—above all, the plants—without the help of agents foreign to the living world. The examination of the means which serve the organisms in chemical reactions naturally presents great difficulties, and even if the way traced by Ciamician is followed by numerous biologists, the actual progress is still slow.

Besides the enzymes, which are the principal catalysts of the organic world, it is necessary to define and study the visible or invisible luminous radiations whose influence on the life process is of main importance. Ciamician had especially in mind the phenomena going on in green plants for which light constitutes the source of energy; he wanted to carry out the transformation of radiating energy into chemical energy as it occurs in plants.

The work which he pursued in this field was accomplished with the help of Paolo Silver who was, during the largest part of Ciamician's scientific career, a valuable collaborator in his devotion and experimental skill.

The phenomena of oxidoreduction, so important in biology, can be reproduced under the influence of luminous radiations by making them act on pairs of conveniently chosen substances, of which one oxidizes at the cost of the other, which then undergoes a transformation in the opposite sense. This is produced in certain cases by simply transposing hydrogen, for instance, making the alcohols react on substances with a carbonyl group: quinones, ketones, aldehydes. Quinone is thus transformed into quinhydrone and hydroquinone under the influence of the alcohol which oxidizes to aldehyde, operating with light under specific experimental conditions. The polyatomic alcohols act the same way, being transformed into sugary substances which are identical with natural sugars; this is, for instance the case with mannitol, which leads to *d*-mannose. The aromatic nitro derivatives are reduced by an identical process in the presence of alcohols and aldehydes, and Ciamician studied particularly the effect of benzaldehyde on nitrobenzene.

The phenomena of autoxidation, polymerization, and condensation can be observed under the influence of light. Also one can find hydrolyses with the opening of closed chains; this is the case

with *o*-methylcyclohexanone, which is transformed at a ratio of 25 per cent into normal heptylic acid and heptylene aldehyde. Menthone and dihydrocarvone undergo similar photochemical changes, and the experiments on the effect of light on odoriferous substances are of evident importance in the theory of the perfume of flowers. Ciamician also studied the condensations of hydrocyanic acid with aldehydes and ketones, hoping to accomplish the synthesis of the amino acids of plants, a problem that greatly interests the biologists.

In collaboration with Ciro Ravenna, professor of agricultural chemistry in Pisa, Ciamician attacked the question of the origin and the transformation of the chemical compounds in plants. Considering the plant organism as a real laboratory, he tried to accomplish syntheses by injecting several products. Among the most demonstrative experiments should be mentioned the synthesis of salicin, which was produced by injecting saligenin into corn plants, a species which does not contain traces of this glucoside in its normal state.

Naturally this question had to lead this scholar to the determination of the rôle of alkaloids in plants. To Ciamician, these compounds do not seem to be residual products of the vegetable metabolism. Instead of eliminating them, the plants modify them and make them more resistant. It would seem that the alkaloids are destined for very specialized functions and constitute genuine vegetable hormones.

The fact that the alkaloids flow toward the injured parts of plants that have been subjected to pinching, for instance, can probably be interpreted as a means by which they try to re-establish, with the help of the alkaloids, the functional equilibrium disturbed by the lesion.

On the other hand, in the kidney bean, the function of the chlorophyll is heightened by an injection of caffeine or theobromine. One observes an overproduction of starch, which does not justify the consideration of the alkaloids simply as waste substances.

Even if certain of Ciamician's conclusions are not in complete harmony with those of physiologists such as Clautriau or Pictet, who have studied this problem, the fact still remains that his researches make a very important contribution toward the knowledge

of the fate of the alkaloids in plants, a particularly captivating question of vegetable biology.

In a last article, published in 1923, in the *Bulletin de la Société de Chimie Biologique*, Ciamician concluded from his work that "the plants practice a chemistry corresponding to what we do in our laboratories; they do it with infinitely simpler means, but with similar intentions. Since their organism is not as differentiated as that of animals, they make up for it with a more perfect chemism."

Ciamician, who taught chemistry of minerals among other subjects at Bologna, was never without interest in the recent problems that arose in this branch of science.

He studied electrolytic dissociation, solid solutions and, in a memorandum published in 1918, relating to "The nature of chemical affinity and the valence of atoms," he developed his views on the fine structure of the atom in perfect accord with the present theories.

This short account shows the great importance and the extension of Giacomo Ciamician's work. He liked to explain his work or the most interesting chemical problems of the present day in brilliant conferences in Italy as well as in France, Germany, Austria, and the United States; in all these countries, he had gained the respect of the scientific world. A profound friendship existed between him and Albin Haller, Emil Fischer, and Henry E. Armstrong. He was a member of all scientific societies in Italy, and of numerous societies outside his own country, and honorary member of the Société Chimique de France.

Among the numerous honorary distinctions which had been granted him in the course of his career, he attached a special value to the Légion d'Honneur, which was bestowed on him by the French government. He was considered, in fact, to be one of the most faithful friends of France in Italy.

In the Italian Senate, where he had a seat from 1910, he was not interested in purely political questions. He gave advice that was always well considered in the discussion of problems of public education or chemical industry. He rendered the greatest services to his country and the Allies during World War I, and he had the good fortune to see his native town, Trieste, become Italian again.

Death brutally put an end to the great activities of Giacomo Ciamician, at the moment when he had a right to look forward to brilliant results of his work; but his work will not be forgotten, and his image will always remain that of a great scholar, who knew how to honor science to which he had dedicated his whole life.

From: *Bull. soc. chim. France*, 4^e s., 41, 1562-66 (1927). Translated by Eduard Farber.

RENÉ FABRE

.. 76 ..

Svante Arrhenius

1859-1927



THERE are two Arrhenius families in Sweden; one was said to have originated in Bavaria. The eminent chemist, Svante Arrhenius, came from the other, from the northern part of the district of Kalmar. The family name is said to be derived from that of the village Årena in the parish Målilla. The branch from which Svante came lived on the Klövdala farm in the parish Jåreda. His uncle, Johan Arrhenius, was a famous botanist and agricultural writer who had contributed markedly to the development of Swedish agriculture by his literary activity and who, for years, was secretary of the Swedish Agricultural Academy in Stockholm. Johan and his brother, Svante Gustaf Arrhenius, were students at Upsala in the 1820's and stayed on there for a time. Svante Gustaf became a land surveyor and later a supervisor of the University of Upsala. Since in the beginning this post brought but little income, he also was employed as overseer in the ancient castle Wik on Lake Målar in the province of Uppland. His wife was Carolina Thunberg of Klövdala; their son, Svante August, was born at Wik on February 19, 1859. Several years later, the father's position improved enough so that the family could move to Upsala where he could devote himself entirely to his university position.

Svante Arrhenius' outstanding abilities manifested themselves early. Of his own accord, and against his parents' wishes, he learned to read at three. At a very young age, he acquired an incredible skill in arithmetic by watching his father add the columns in the account books. This early knowledge of numbers is particularly interesting if it is recalled that, in his future work, he especially liked to discover relationships and laws in masses of observational data. When he was eight, he entered the fifth grade of the Cathedral School. Although the youngest in his class, he was superior to most of the others with respect to information and ability. He did particularly well in physics and mathematics. M. M. Floderus, the principal of the school, and the author of the physics text then most widely used in the schools, taught this subject. He had a high opinion of the young Arrhenius, who finished school in 1876, at the age of seventeen.

Svante Arrhenius, therefore, was not one of the great number of famous scientists who were more or less irked by school and made poor scholastic records, like Liebig and Berzelius. The latter, for instance, came to Upsala from the gymnasium in Linköping, with a certificate in which the principal had noted that he "was a young man with good natural abilities, bad manners and questionable expectancy," a certificate which weighed heavily on the boy's spirit. If an explanation of this rather common occurrence is sought, it may be that it involves young men of quite specialized interests, whereas Arrhenius, as was gradually revealed, had very extensive interests. In this connection, it may also be pointed out that Arrhenius—in contrast to many Swedish scientists—had practically no financial difficulties during his student days, a condition furthered by his pronounced thrift.

After graduation from secondary school, he embarked on his university studies for the first state examination, studying mathematics and chemistry, followed by physics. He became a candidate for the bachelor's degree at Upsala in 1878. Then followed, again at Upsala, the examination for the intermediate degree, the licentiate in philosophy, as well as the doctoral disputation.

Arrhenius was not as satisfied with his chief instructor in physics at Upsala as he had been in secondary school. Tobias R. Thalén (1827–1905) was known as an eminent and competent experimental physicist and an excellent lecturer. Consequently, the dissatisfaction could not have been due to any incompetence of this teacher. Arrhenius, in his autobiographical notes published in connection with the presentation of the Nobel Prize for Chemistry (1903), stated that the practical instruction in physics at the time (1881) was deficient. Otto Pettersson, who was professor of chemistry at the University of Stockholm from 1881 to 1908, stated in an interesting article regarding this Nobel Prize: "The 80's were not a favorable time for those who wished to do experimental work in physics at Upsala." Thalén's notable achievements did not prevent him from giving scant encouragement to young researchers in his laboratory, and he showed but little inclination to secure the necessary equipment for them. Moreover, the apparatus for the usual physics exercises was scanty. A more serious reason why Thalén and Arrhenius did not get along with one another was

because of their entirely opposing points of view; Thalén placed the main emphasis on exact experimental studies, whereas Arrhenius was always expounding new hypotheses. He was ready to test them by approximate experiments, but he had no desire to make tedious accurate measurements, since it was his goal to obtain a general view of hitherto unknown relationships quickly from approximate experiments.

Arrhenius left Upsala as early as 1881 in order to continue his training in physics at Stockholm under E. Edlund, the physicist of the Swedish Academy of Sciences. In him, Arrhenius found a teacher to his tastes, and it is reported that "Edlund was soon prepossessed by Arrhenius' method of working and later greatly furthered his interests." He gladly placed at the young man's disposal the wealth of apparatus belonging to the academy so that the experimental studies relating to the doctoral research could proceed.

In his doctoral thesis of 1884, and also in a rather short paper published in 1887, Arrhenius already was discussing the electrolytic theory of dissociation, which soon was to prove so fruitful and to become his greatest accomplishment. Here is another instance demonstrating that the best ideas of leading men are often found in their early studies. Arrhenius was only twenty-five when he published his famous doctoral work.

This dissertation was written in French and has the title: "*Recherches sur la conductibilité galvanique des électrolytes.*" It makes up Papers 13 and 14 in Volume 8 of the Supplement of the Acts of the Royal Academy of Sciences, printed in 1884. These papers had already been announced at the meeting of the Academy on June 6, 1883, and accepted for publication; later they were combined to form the doctoral dissertation. The first part (No. 13) has 63 pages and No. 14, the second part, occupies 89 pages in Volume 8, cited above.

The first part begins with an account of the experimental studies conducted in Edlund's laboratory; they provide the basis for the theoretical presentation. These investigations dealt with the determination of the electrical conductivity of electrolytes at high dilutions, to 0.0005 normal or less. Heinrich Lenz (1804-65) professor of physics in St. Petersburg, and Friedrich Kohlrausch

(1840–1910) had made similar measurements in the 1870's, but these did not extend to such great dilutions as Arrhenius thought necessary for his purposes.

The third and last chapter of the first part bears the title "Theory." The new theoretical views were formulated in 56 theses, which, with consecutive numbering, go through the entire work, each thesis being preceded by a statement of its basis. The reader of these theses is struck by the admirable acumen and the well-considered judgment with which most of them are formulated, particularly if it is remembered that the data available for their derivation were very scant in comparison to what was subsequently brought to light because of these theses. With discerning clear-sightedness, the originator combines separate phenomena and provides them with a concentrated explanation. Only a few of the theses have not stood the test of time or have had to be greatly modified.

The first thesis states that, for very dilute solutions, the electrical conductivity of a solution of a salt is proportional to the concentration, other conditions being the same. The second states that the conductivity of a dilute solution of two or more salts is continuously equal to the sum of the conductivities which a solution of each of the salts would have at the same concentration. According to theses 7, 8, and 9, respectively, the electrical resistance of an electrolyte solution rises with increases in: (1) the internal friction; (2) complexity of the ions; and (3) the molecular weight of the solvent. This last thesis is an example of those propositions that have not been completely confirmed. Besides the internal friction of the solvent, Arrhenius also considered another factor related to the nature of the solvent; it is, however, as is known now, not the molecular weight of the solvent but its dielectric constant that is of significance in this connection. His statement can be explained—he worked only with a limited number of solvents: water, several alcohols, ether—for which it is approximately true that the dielectric constant decreases as the molecular weight rises.

Whereas the thirteen theses advanced in the first of the papers were set up mainly on the basis of actual experiments, with no accompanying hypotheses for their explanation, the second part

(No. 14 in Volume 8 of the Supplement) bears a more pretentious title "Théorie chimique des électrolytes." Here can be found the explanation of the results given in Part I and the bold structure of ideas which came to be known as the theory of electrolytic dissociation.

In thesis 15, it is stated first of all, but only for a solution of a hydrate, that the latter consists "in addition to water, of two constituents, namely an active (electrolytic) part and an inactive (nonelectrolytic) part," and, further, that on dilution of the solution the active part increases and the inactive part decreases. This is then extended to other dissolved electrolytes (salts): "The activity coefficient is a figure which gives the ratio between the number of ions actually present in the electrolyte to the number of ions which must be present there if the electrolyte should be completely transformed into simple electrolytic molecules." Here, as was his custom, Arrhenius employs the term *electrolyte* to denote the solution as a whole, while he otherwise and also, as can be seen, immediately thereafter uses this term to denote the dissolved materials (salt, acid, base) from which the conductivity stems. Consequently, the activity coefficient is the same as the degree of electrolytic dissociation, and the active (electrolytic) part is the same as the ions. His expressions, *active* and *activity coefficient*, naturally are reminiscent of Guldberg and Waage's *active mass*. It is likely that Arrhenius obtained the idea for his terms from the writings of these Norwegians; he frequently cited their publications, which, at that time, were still unappreciated. Arrhenius later stated that he, too, did not know of this work until quite late in his own investigation. The meanings which he and they ascribe to *activity* are not identical but are closely related.

Arrhenius himself pointed out that his theory was not without predecessors. In this connection, he cited such eminent authorities as Alexander Williamson (1824–1904) of the University of London, and the physicist, Rudolf Clausius (1822–88) at Bonn. The former had touched on this field in 1851, and, in 1857, the latter had advanced the hypothesis that a dissolved salt is dissociated to a certain extent into its two mobile ions even though no current is passing through the solution.¹

Thus, the pre-existence of ions in the solution had been presented previously, at least by Clausius and in fact later (1921) Arrhenius stressed that Gay-Lussac had advanced similar ideas as early as 1839. In his well-known theory of the formation of ethyl ether on heating alcohol and sulfuric acid, Williamson does not speak of ions, but only of radicals (fragments of molecules) and does not attribute any electrical charge to them.

The question has been raised as to whether Arrhenius should really be credited with the fundamental development of the theory of electrolytic dissociation. The answer is definitely "Yes," and for the following reasons: Clausius, as was indicated above, limited himself to stating that a small part of the salt must be split beforehand into ions, but he did not state or calculate how much of the salt is thus affected.

The essential advances that we owe to Arrhenius reside in the appreciation that the salt, in many instances, is largely split into ions before any electric potential is applied to the solution. He stated how the extent of the splitting of the salt into ions can be computed quantitatively. This procedure is not to be found in the doctoral dissertation which is being discussed here, but in the paper of 1887 which will be taken up later.

The chemical applications begin after thesis 15. Thus we find the pregnant statement: . . . "The strength of an acid is the higher, the greater its activity coefficient (its molecular conductivity). The same holds true for bases." In thesis 31, it is asserted that the dissociation becomes complete at infinite dilution of the solution and, in 34, that in solutions of the salts of weak acids, strong acids displace the weak acids.

Although the Clausius pronouncement did not necessarily have a revolutionary effect on the chemical ideas of the time, this was by no means true of the views put forth by Arrhenius. Three objections in particular were raised. The first was the difficulty of comprehending how sodium chloride, for example, which was customarily regarded as a particularly stable material, could be split into its components (more precisely, into its ions) by merely dissolving it in water. The obvious answer to this was that this spontaneous process is no more remarkable than the accepted fact

that solid sodium chloride, which is not significantly volatile at room temperature, dissolves readily in water and thus spreads throughout the liquid as a gas does in an empty space. The second one was: How is it possible for free sodium to be present in an aqueous solution when metallic sodium violently reacts with water, or how can free chlorine be present in the colorless, odorless solution, since a water solution of chlorine is yellow and has a penetrating odor? The response to this question was that sodium ions and chlorine ions are not the same as metallic sodium or chlorine gas. Both of these ionic species are electrically charged in contrast to the free elements; furthermore, the chlorine ion consists of only one chlorine atom, whereas molecules in chlorine gas contain two atoms. The third objection was that the sodium and chlorine ions should be capable of being separated by diffusion; this actually is possible to an extent, although the electrical forces oppose the separation so potently that the diffusion can be detected only by virtue of the resulting electrical charges of the solution or water, not by chemical means.

However, some Swedish chemists approved of the research. These included Otto Pettersson, then professor at the Technical University in Stockholm, and A. G. Ekstrand, then docent in chemistry at Upsala and later editor of the *Svensk Kemisk Tidskrift*. On the other hand, Thalén had a low opinion of the work, and even Per T. Cleve (1840–1905), professor of chemistry at Upsala, was said to have been quite hesitant in his appraisal. As a result, the paper itself was given the mark *non sine laude* and the defense was graded *cum laude*. According to the then prevailing custom, this was not sufficient to qualify the candidate for a docentship; *cum laude* would be required for both the dissertation and the defense. It is reported that a later inquiry regarding the granting of a docentship was definitely rejected.

This appraisal of the doctoral work was long a topic for discussion. Considering the difficulties in judging revolutionary views, together with the fact that the available experimental data were not especially satisfactory, and also that the presentation is not always easy to follow, the verdict was not too surprising. Fortunately, this failure had no serious consequences.

Wilhelm Ostwald, who was then professor at the Polytechnikum in Riga, came to Upsala in the summer of 1884. He had already worked in the field of physical chemistry; among other things, he tested the Arrhenius theory of the relationship between conductivity and reaction velocity on 34 acids and found that it held true. He was anxious to meet the author of this theory. In his introduction to the volume of the *Zeitschrift für physikalische Chemie*, issued in 1909 to commemorate the twenty-fifth anniversary of Arrhenius' doctorate and the electrolytic dissociation theory, Ostwald wrote: "Along with several contestable views it [the dissertation] contained so many and such profound new thoughts that I was soon convinced of their fundamental importance." On his visit in 1884, he spoke to the authorities in Upsala in very favorable terms concerning the dissertation and later reported:

I can still plainly recall the scene in the chemical laboratory in Upsala, where the head [Cleve], himself an eminent chemist, heatedly asked me, pointing to a beaker containing an aqueous solution—"And you too believe that sodium atoms are swimming around there in this fashion?" When I agreed, he quickly looked at me in such a manner as if he had considerable doubt about my chemical rationality. However, this did not prevent the esteemed older colleague from receiving us both with true Swedish hospitality, and later he did what he could to remove the difficulties surrounding the granting of the docentship.²

Ostwald himself offered Arrhenius a place at Riga, with the result that an application for docentship in physical chemistry at Upsala was acted on favorably. The appointment was to start at the end of 1884. In September, 1884, Arrhenius accompanied Ostwald to a scientific congress at Magdeburg, and they planned to go from there to Riga in order to lay out a program of studies in physical chemistry. However, Arrhenius had to return home because his father was seriously ill. The latter died in 1885.

Arrhenius soon left Upsala again. Through the influence of Edlund, he received a travel grant from the Swedish Academy. This sum (4500 Swedish crowns) plus his own means enabled him to enjoy a number of years of travel and study. He worked

with Ostwald in Riga; with Kohlrausch in Würzburg (1886), where he became acquainted with Walther Nernst; with Ludwig Boltzmann (1844–1906) in Graz (1887); with van't Hoff in Amsterdam (1888); and again with Ostwald, who had been called to Leipzig in the meantime. These years were filled with intensive and most fruitful work, and, to use an expression probably coined by Arrhenius himself, "the dissociation theory matured." These were also joyful years—not only because he was happy in his work, but also because of the pleasure that came to him from his natural jovial nature and humor, which made him a favorite among so many of his friends and associates. He had the opportunity to become acquainted with the leading men in his field in Central Europe, and the fact that he was almost generally called "Svante" indicates how well he was liked.

The summer and fall of 1888 were spent in Sweden. Part of the time, he worked with Edlund until the latter died in August, and in the fall semester, he lectured on physical chemistry at Upsala. Here, for the first time, the new theories were set forth in connected form before an extremely interested audience. The years 1889 and 1890 found him abroad again. Most of this time was spent at Leipzig, where he served as assistant during the summer semester of 1889. He also was at Graz for a while.

During this period, an event occurred which was of vital interest to chemistry in general and to the completion of the dissociation theory in particular. This event was the publication of the famous paper by van't Hoff on "*Lois de l'équilibre chimique*," first in the *Archives Néerlandaises* and then in more extended form in the *Transactions of the Swedish Academy* of 1886. In this research, van't Hoff encountered a great difficulty which he could not explain. Solutions of salts, acids, and bases possess a greater osmotic pressure, higher vapor tension, and larger depression of the freezing point than the calculated values. It should be noted that, of course, no splitting of the salt into ions had been assumed in these calculations. Accordingly, van't Hoff had to limit his statement and declare that the laws of osmotic pressure and the related phenomena applied to a "majority of compounds." The great class of electrolytes (salts, acids, bases) had to be classed "exceptions."

This great difficulty was resolved, and the theory of electrolytic dissociation was given its quantitative formulation, in the paper which first appeared in the *Ofversigt* (Review) of the *Transactions of the Swedish Academy* for the year 1887 under the title "Attempt to compute the dissociation (activity coefficient) of compounds dissolved in water" (10 pages).³ The term "activity coefficient" appears in parentheses; in other words, Arrhenius now takes off the mask and plainly states that the fission products of the dissolved salts are its electrically charged ions.

Arrhenius here proceeds on the assumption that an osmotic pressure must be ascribed to the dissolved ions. "In the paper [his doctorate dissertation] referred to above, I have termed those molecules whose ions move independently of each other, active, and the other molecules, whose ions are closely bound to each other, inactive. Likewise, I have raised the possibility that, at infinite dilution, all inactive molecules are converted into active ones. I will make this assumption the basis of the following computations. I have denoted as activity coefficient the ratio between the number of active molecules and the sum of active and inactive molecules. Accordingly, at extreme dilution, the activity coefficient of an electrolyte will be unity. At low dilutions, it will be less than one and, in accord with the principles stated in the cited work, for not too concentrated solutions [solutions where disturbing influence due to internal friction, etc., can be neglected] it can be placed equal to the ratio between the actual molecular conductivity of the solution and the upper limiting value, which the molecular conductivity of this solution approaches at extreme dilution."

The degree of electrolytic dissociation was then quantitatively calculated by the formula:

$$\alpha = \Lambda / \Lambda_{\infty}$$

in which: Λ = the molecular (or equivalent) conductivity at the given concentration and Λ_{∞} denotes the limiting value, to which: Λ approaches asymptotically with rising dilution. Furthermore, the formula for the so-called isotonic coefficient, i , is derived, i.e., the ratio between (1) the actual osmotic pressure or the de-

pression of the vapor pressure, elevation of the boiling point or lowering of the freezing point of the solution and (2) the value which is calculated in case there is no splitting into ions:

$$i = 1 + (n - 1) \alpha$$

in which n denotes the number of ions into which a molecule splits. Thus, the "exceptions" to van't Hoff's law were explained at once, and the two values of the degree of dissociation, which thus could be derived from such diverse groups of phenomena as the electrical conductivity, on the one hand, and the osmotic pressure and the dependent values, on the other, exhibited a brilliant agreement, through which once more the theory of electrolytic dissociation received substantial confirmation. These papers of 1884 and 1887 represent the core of Arrhenius' most distinguished work in chemistry.

Two other theories influenced the revolution that was initiated by the work of Arrhenius and van't Hoff. The first was the Guldberg and Waage law of mass action, which had been formulated in 1867; it had not previously received deserved attention, but now its significance became apparent. The second was Nernst's theory of electromotive force (1888) which rests on the theory of electrolytic dissociation and the theory of osmotic pressure. Arrhenius' discoveries were made possible by the work of mainly two men, Friedrich Kohlrausch (1840-1910) and Wilhelm Hittorf (1824-1914). Kohlrausch had developed a method which was generally applicable for measuring the conductivity (resistance) of electrolytes and, in addition, had made extensive and accurate measurements. The fundamental work of Wilhelm Hittorf, whose studies of the migration of ions (1853-59) had been mostly disregarded at the time, had been cited by Arrhenius. Of course, Hittorf did not assume that free ions pre-exist in the solution; he believed that they are formed only when an imposed electric tension separates the molecules into their ions. He obviously could then speak of the mobility of these fragments.

The discoveries of van't Hoff were based on the experimental material gathered by Pfeffer and Raoult. In this connection, it should also be remembered that as early as 1870 Guldberg had de-

duced the connection between the lowering of vapor pressure and depression of the freezing point in the case of solutions, so that van't Hoff's discovery can be linked more accurately with the discovery of the laws of osmotic pressure and its relation to vapor pressure, boiling, and freezing points of solutions. Mention has already been made of the principle assumptions which served as the basis for Nernst's theory of electromotive force.

In a certain sense, the theory of electrolytic dissociation is a pattern for the modern theory of the transport of electricity through gases and opened the way for the latter, thereby, in great measure, contributing also to the development of the atomic theories of the present time. Another significant result of general nature is the erection of a bridge between physics and chemistry, i.e., the search for causes that are common to physical and chemical events.

The introduction of the theory not only required much work but also brought on heated conflicts between the champions of the earlier chemistry and the "wild horde of the Ionians" as the adherents of the newer views were sometimes called. It cannot be stated exactly how long the strife lasted, but the fact that the Nobel Prize in chemistry was given to van't Hoff in 1901—the first time it was awarded—and then to Arrhenius in 1903 "for the extraordinary service which he rendered to the development of chemistry through his theory of electrolytic dissociation" may be taken as the official close of the battle. At the banquet following the presentation of the prize, the first conferred on a Swede, Cleve delivered a fine tribute in which he recalled the countercurrents which were directed against the new views at the beginning.

In 1891, Arrhenius received a call to the University at Giessen but chose instead a post in physics at the Technical University of Stockholm offered to him in September, 1891. This post was converted into a professorship of physics in 1895, a promotion that was not without difficulties. He occupied this chair until 1905, when he became head of the physical chemistry division of the Nobel Institute of the Academy of Sciences.

During the period at the Stockholm University, a stream of students from home and abroad came to Arrhenius, the greatest such stream since the time of Karl Linnaeus (1707–1778) and J. J. Berzelius (1779–1848). Among the foreigners to learn from Ar-

rhénus were: Richard Abegg, Georg Bredig, Viktor Rothmund, Ernst Cohen, Harry Jones, Thomas Madsen, Hans Euler, and many others.

Besides membership in numerous Swedish scientific societies, including election to the Academy of Sciences in 1901, honorary memberships were also conferred by many foreign academies and societies. In 1902 he was given the Davy Medal of the Royal Society of London.

From 1902 on, Arrhenius applied the laws of theoretical chemistry to Physiological problems, especially those of serum therapy (immune chemistry). Comprehensive surveys were published in his "Immunochemie" (1907) and his "Quantitative laws in biological chemistry" (1915). His studies in these fields were met with resistance at first by Paul Ehrlich and his school, but their fundamental importance became more and more evident as time went on.

Among his numerous studies of cosmic physics are the joint publications with N. Ekholm concerning the northern lights and the hypothesis that the ability of radiation pressure to transport cosmic material can be used to explain comets, the corona, polar aurora, and the zodiacal light. Here also can be found his idea that spores of living matter are transported in this manner from planet to planet with the resultant spread of life throughout interstellar space. He also developed a theory designed to explain the ice ages and other great climatic changes experienced by the earth's surface. This theory is based on the ability of carbon dioxide to absorb the infrared heat radiation sent out from the surface of the earth. In periods of intense volcanic activity, the carbon dioxide content of the atmosphere is increased so that the heat radiated from the earth's surface is held back more and the temperature of the atmosphere rises; the reverse holds for periods of weak volcanic action. The content of water vapor in the atmosphere, which rises and falls with the temperature, acts in the same direction and consequently reinforces the result. The vegetation, which is dependent on the temperature, acts as a regulator. However, it was not possible to bring this hypothesis into complete agreement with geological chronology. His "Lehrbuch der kosmischen Physik" (2

volumes) first appeared in 1903; in this he set forth his bold speculations.

During later years Arrhenius wrote several textbooks and works of a popular nature which, like his scientific writings and researches, tend to testify to his extraordinary productivity and capacity. In 1898 he published his "Lehrbuch der theoretischen Elektrochemie" which was translated into many languages. The text is not easy to read; in general his style is very concise and somewhat heavy. He made it a custom to indicate what was still to be done in the fields about which he was writing. His "Theorien der Chemie" (1906) is likewise characterized by this admirable conciseness. Among his many books written for the general public was "Die Chemie und das moderne Leben" (1919). In the introduction he states that the chief motive for writing this book was that the war had demonstrated the special importance of chemistry and that this science more than any other was serving the material culture of the time.

Other books revealed to the general public the main features of cosmic physics and cosmogony; of course, he stressed his own ideas and views. Among these volumes were "Das Werden der Welten" (1906: 8th edition, 1924); "Der Mensch vor dem Welträtsel" (1908); "Die Schicksale der Sterne" (1915). Most of these comprehensive and popular works appeared during the time he was head of the Physical-Chemical Section of the Nobel Institut in the outskirts of Stockholm. New researches were also being conducted in this laboratory. Many men who later became prominent scientists worked there under his guidance.

His first marriage was to Sofia Rudbeck. Their son, Olev Wilhelm (b. 1895) became a botanist and made important contributions, especially on the importance of soil acidity with respect to the culture of sugar beets. Three children were born of his second marriage to Maria Johansson.

Arrhenius had a natural, healthy constitution but he never spared himself. In his later years he was head and member of several large organizations and was so in demand that he found it difficult to find time for scientific work. Consequently, beginning in 1925, he made it a practice to arise at 4 A.M. in order to steal a few peaceful hours with which to work on the new edition of his

"Entwicklung der Welten." This extra effort may have contributed to the first attack of weakness that struck him near the end of 1925. His full powers never returned. In the spring of 1927 he therefore resigned his post as director of the Nobel Institut. The Academy of Sciences granted him an honorary pension. During the summer of 1927, he wrote his memoirs. After a brief illness (acute intestinal catarrh), which laid him low in September of that year, he died in October 1927. He was buried in Upsala, the city in which he grew up and where he had fought the opening battles of his crusade in behalf of his theory of electrolytic dissociation.

GENERAL REFERENCES

- "Nobel, the Man and his Prizes," edited by the Nobel Foundation, Sohlman's Förlag, Stockholm, 1950.
- Svante Arrhenius, "Worlds in the Making," Harper, New York, 1908.
- H. C. Urey, "The Planets: Their Origins and Development," Yale University Press, New Haven, 1952.
- H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York, 1957.
- Hans von Euler, "Arrhenius," in *Chem. & Ind. (London)*, 1959, 245.
- E. Riesenfeld, "Arrhenius," in *Ber. deut. Chem. Ges.*, 63A, 1, (1930)

NOTES AND REFERENCES

- 1 A. W. Williamson, *Ann.*, 77, 37 (1851); 81, 73 (1852); R. Clausius, *Pogg. Ann.*, 101, 338 (1857).
- 2 W. Ostwald, *Z. physik. Chem.*, 69, IV (1909).
- 3 Also published in German in *Z. physik. Chem.*, 1, 631 (1887).

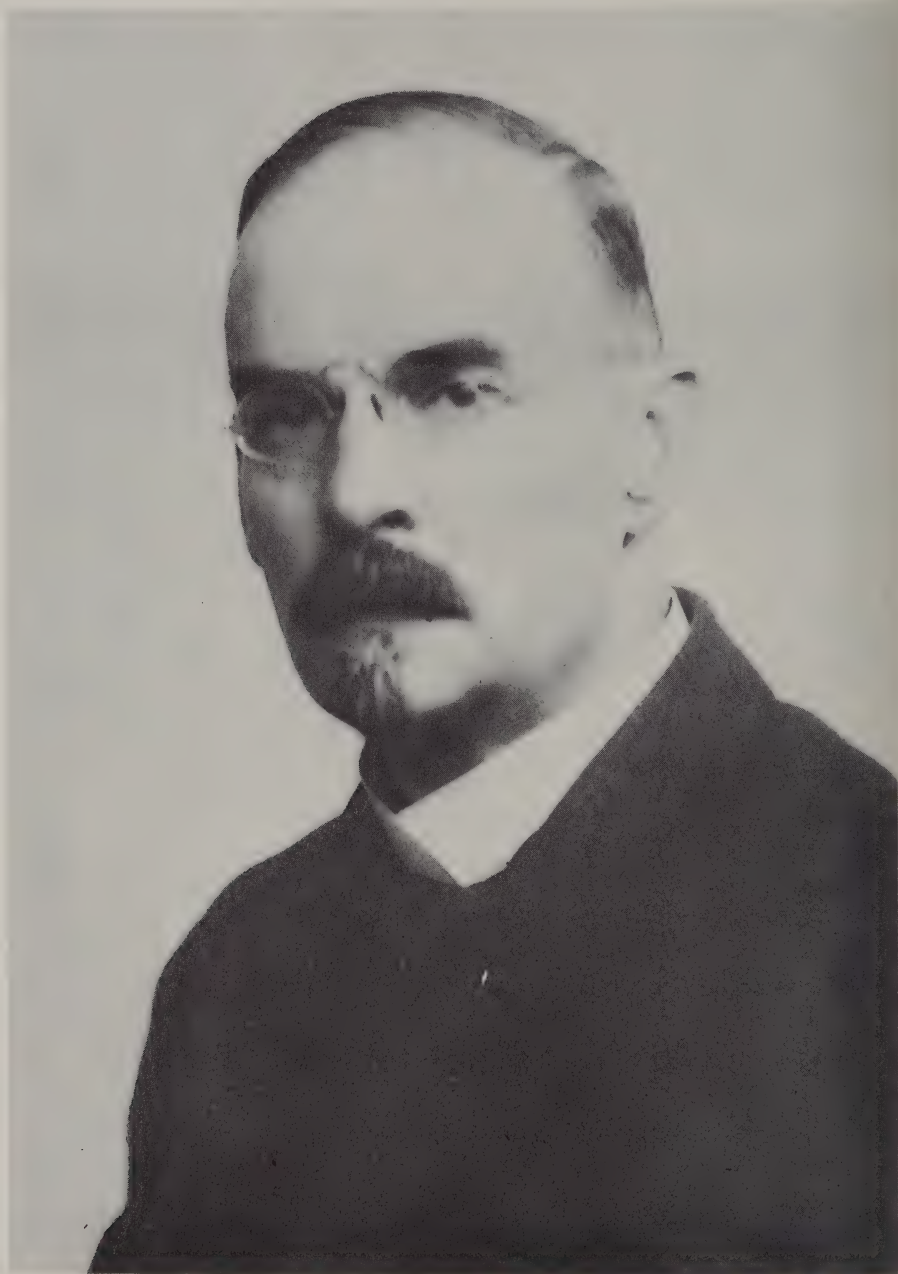
From: Bugge, "Buch der Grossen Chemiker," 2, 443-462. Translated and abbreviated by Ralph E. Oesper.

WILHELM PALMAER

.. 77 ..

Ossian Aschan

1860-1939



ADOLF OSSIAN ASCHAN was born May 16, 1860, at Helsinki (Helsingfors). His parents were Karl Achates Aschan, a teacher of zoology and botany and vice-rector at a lyceum, and Mathilde Helena Waenerberg, the daughter of a ship's captain. Through them he inherited characteristics of the two nationalities in Finland, the Finns and the Swedes. From his father's side he received a heritage of scientific ability, documented by the professions of his paternal ancestors. From his mother he inherited diligence, tough persistence, and the ability to organize his work skillfully, as he said himself in an autobiographical sketch.

When Ossian had to choose his life's profession he did not select science. His brother Allan became an apothecary, like others by the name of Aschan before him. Ossian became a student of bridge, road, and water engineering at the Polytechnical School in Helsinki. In the Finland of that time the study of science offered no prospects except to teach, as his father did; chemistry as a field of study was still less promising in a country that had practically no chemical industry. However, in order to have the necessary scientific foundation for his engineering studies, he attended lectures on mathematics, physics, and chemistry at the University.

Chemistry as a science was not well represented in Finland at that time. Gadolin's successor in the chair of chemistry was Chydenius, who was seriously ill for many years so that he could not teach. Besides him there was only one lecturer in chemistry, Wahlforss, who pursued inorganic chemistry and remained out of step with the new organic chemistry. However, Wahlforss was an outstanding teacher, and it was mainly through his influence that Aschan found his way to chemistry.

In 1881 Aschan left the Polytechnic Institute as a chemical engineer and, at the same time, obtained the degree of *magister philosophiae* at the university. Then followed practical work in chemical industry, first in a saltpeter plant in Turku, and next in a dye works in Petersburg. The director of the latter advised him to take a course in dyeing given in Berlin. Aschan used this oppor-

tunity to study with August Wilhelm von Hofmann at the university. The investigation started there was completed in Stockholm and led to the doctor's degree in 1884. After returning to Helsinki he was engaged as a geologist and as the director of a municipal laboratory for food analysis.

In 1887 Aschan started work in the field of alicyclic compounds, which was to occupy him all his life. It was not a special scientific inclination that led him to these compounds; up to that time he had tried his hand on topics of aromatic chemistry. The stimulation came from the outside; it was the same that had influenced Wladimir Wassiljewitsch Markownikov ten years before and now induced Nicolai Dimitrijewitsch Zelinsky, who was of about the same age as Aschan, to study this field. The problem was to exploit the vast naphtha reserves of Russia as advantageously and completely as possible. Russian industry had approached Markownikov with the request to find out what substances were present in Caucasian mineral oil and how they could be separated. For Aschan the problem was the more specialized one of finding uses for the naphthenic acids remaining as residues from naphtha distillation. This is an example for the frequently encountered fact that progress in chemical research is by no means always aimed in the direction toward logical developments but is influenced by technical problems more strongly than other branches of science. It became soon evident that a technical solution of Aschan's task could not be reached immediately. Aschan recognized that, first, a very thorough scientific investigation was required before anything technical could be developed.

In order to be better equipped with the experimental techniques needed for this task, Aschan journeyed again to Germany in 1890. He worked with Johannes Wislicenus in Leipzig and with Adolf von Baeyer in Munich. In 1894 we see him again in Germany, with Victor Meyer in Heidelberg, where he also met J. W. Brühl. Together with Brühl, Aschan worked on Roscoe-Schorlemmer's textbook of organic chemistry, and from him he obtained first-hand knowledge of the importance of the physical properties of organic compounds for elucidating their chemical constitution.

In the meantime, Aschan's first fundamental study of cam-

phoric acid was completed in 1893, and work on a Swedish textbook of organic chemistry was completed with Edvard Hjelt. An extensive dissertation on structural and stereochemical studies in the camphor group appeared in 1895. It contained new experiments and a critical survey of all previous work on the structure of camphor. He weighed the theoretical conclusions from the experiments with great caution. He could not accept Bredt's formula for the constitution of camphor because a few reactions were not in accord, although none definitely contradicted it. A few years later he reviewed the problem again and in 1903, he decided in favor of Bredt's formula.

In 1898 Aschan became a teacher at the Polytechnic Institute, and in the following year he substituted at the University for Edvard Hjelt, who had been elected rector. Aschan was well prepared for extensive tasks in teaching, because in addition to the Swedish book on chemistry (with Hjelt) he published the "Ausführliche Lehrbuch der Chemie von Roscoe-Schorlemmer" with Brühl and Hjelt in the years 1896 to 1901. His book of over 1000 pages on alicyclic compounds appeared in 1905; for it he was awarded the Vahlbruch Prize, amounting to 10,000 marks, from the University of Göttingen. How great this honor was can be judged from the fact that its first recipient, in 1898, had been Wilhelm Conrad Röntgen.

In 1908 Edvard Hjelt resigned as professor to become a senator and devote himself to political activities for Finland. Thus, the professorship in which Aschan had acted as a substitute became vacant. At that time Aschan was in Berlin as director of the scientific laboratory of the Chemische Fabrik auf Actien, vorm. E. Schering. Now his country recalled him, and he followed gladly.

The main part of his experimental work was concerned with camphene and the group related to fenchone. At the same time he started on a problem of as much scientific as technical importance, the polymerization of isoprene to rubber.

This research paralleled efforts to maintain the national Finnish spirit at the University against the encroachments by the Russians. Aschan's interest in political events was so great that he accepted the election to the Finnish parliament as representative of the

Swedish Popular Party. He was a member in the central organization of this party from 1910 to 1916. In addition, he also was a representative in the city council

The events of World War I gave a new direction to his experimental work. In 1916 it became urgently necessary to reduce the amounts of rosin and alum in sizing paper. The research on this problem led to extensive work about the pine rosin acids, $C_{20}H_{30}O_2$. Although their existence had been known for almost a hundred years, none of the rosin acids described in the literature could be said to be chemically pure. The first success was achieved in work with Finnish talloil, the by-product obtained from the cooking liquor used in the manufacture of sulfate cellulose from pine wood. From talloil, a pure acid, pine abietinic acid, was isolated. Upon Aschan's suggestion, Artturi I. Virtanen tried to determine its chemical nature. By converting the chloride of this acid into the hydrocarbon, retene, Virtanen was able to develop a preliminary structural formula.

In 1916 Aschan also laid the groundwork for a central laboratory for the chemical industry in Finland, and he furthered its development as a director and consulting chemist. He endeavored to make his inventions useful to his country; among other things, he proposed that his experiences in producing and polymerizing isoprene be offered to Germany in exchange for bread flour. The proposal was, however, not carried out.

After the end of the war, Aschan had the good fortune to remain active as a professor for about ten more years. He retired in 1927, but even then he continued his scientific research. None of his predecessors had represented the science of chemistry at the State University as long as he had, except for Johann Gadolin (1760–1852), the first Finnish chemist at the University which at that time was located at Turku. The number of Aschan's pupils and, through them, his influence on chemistry in Finland, was very great.

Scientific and industrial organizations showed their great appreciation for his achievements. Many honors came to him. His collaboration with the German firm of Schering has already been mentioned. After the world war, the Hercules Powder Company

of Wilmington, Delaware, and its subsidiary in Rotterdam, Holland, invited his collaboration.

In view of his great scientific and technical accomplishments, it might appear as if there could not have been much time for other pursuits. However, as has already been mentioned, he was politically active in parliament and in the city council. He did more for the public. Especially noteworthy were his efforts against prohibition. An organization, over which he temporarily presided, fought against such a law because its circumvention could be more harmful than the dangers involved in a moderate use of alcoholic beverages. He recommended educating the people without legal prohibition.

Finally, Aschan even found time for his private hobbies. He liked music. He was a member, for a time even president, of a choir and of the Swedish Oratory Society. His musicality was inherited particularly by his daughter Inger, the youngest of three daughters. His wife, Elin, whom he married in 1885, was the devoted companion of his life until he died February 25, 1939.

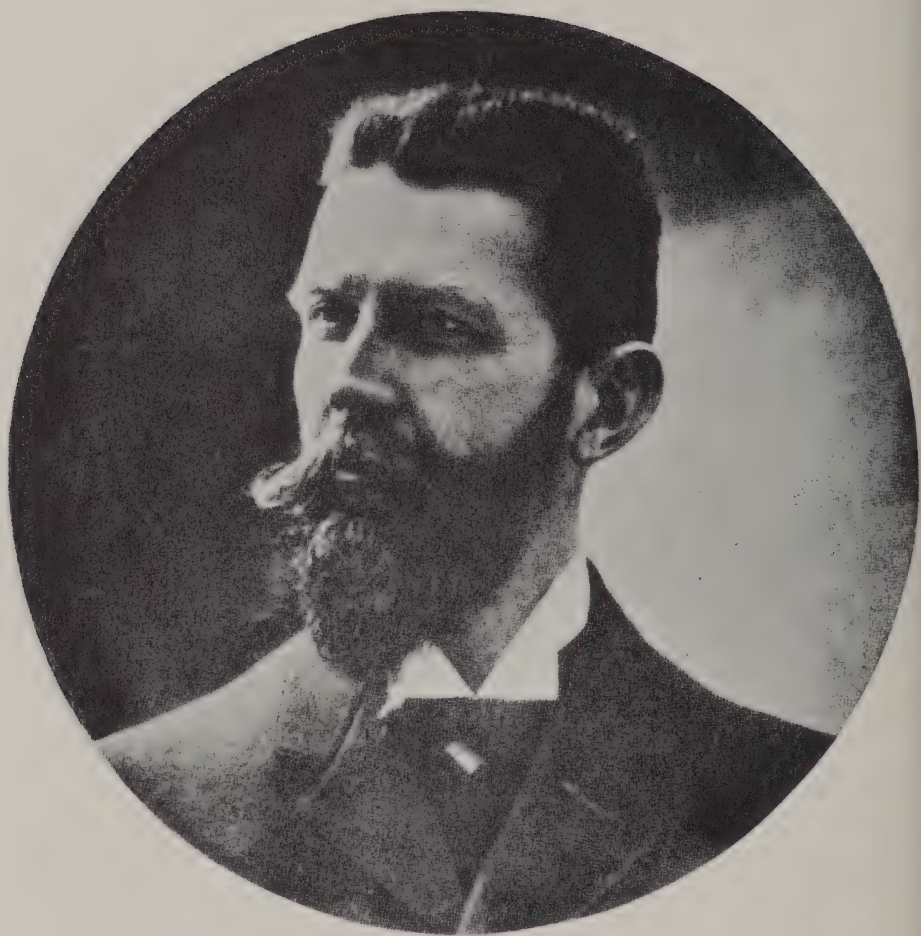
From: *Ber. deut. chem. Ges.*, 74A, 189 (1941). Translated by
Eduard Farber.

WALTER HÜCKEL

.. 78 ..

Philippe-Auguste Guye

1862-1922



IN THE afternoon of March 27, 1922, the brilliant intelligence and great heart that was Philippe-Auguste Guye was extinguished. The news of his death caused painful surprise; most of us did not expect it. We knew that Guye had neglected his health. He carried on so many tasks that it would have overburdened the strongest men: the preparation of his lecture courses and the direction of his laboratory, with all that this implied in research, discussions, and editorial work; the direction of the *Journal de chimie physique* and that of so many commissions and councils; the maintenance of a flood of correspondence, because it was never in vain when one addressed this discreet and warm-hearted man. Everybody wrote to him on scientific questions as well as for advice or support. He never left a letter unanswered, and he did not neglect the innumerable duties he had accepted. Rising early, retiring late, he experienced fatigue at a relatively early age. About twelve years before his death he had a breakdown which he mastered after a rest cure. Some time later again he felt tired but did not cease to devote himself to others. Last December he took a vacation and went south, but his stay there did not produce the desired result. Guye returned to Geneva still weaker and passed away, spent by constant work, before he reached sixty.

Philippe-Auguste Guye, a citizen of Geneva, was born at Saint-Christophe (Vaud) the twelfth of June, 1862. He studied in Geneva and obtained his doctor's degree there in 1884. As an assistant to Carl Graebe (1841–1927) and privatdocent (1885) he published several papers on organic chemistry with Graebe. Then Guye went to Paris where he dwelt until 1892. He always remembered vividly and gratefully these years in Paris during which he found himself through contact with eminent scholars. He particularly recalled being influenced by Charles Friedel (1832–1898, successor of Adolphe Wurtz).

The reputation of the young scientist preceded him to Geneva, where he returned in 1892 to take charge of the associate professorship in theoretical and technical chemistry, which had been

established especially for him and was transformed into a full professorship in 1895. He remained in this post until he died.

Guye's scientific work comprised almost 200 papers in his own name and more than 600 publications from his laboratory which were directly inspired by him. It is, therefore, impossible to do more than just indicate the essential traits of such a vast productivity.

His first problem was that of the rotatory power of optically active substances. The principles which Pasteur had formulated concerning the asymmetric carbon atom had been spectacularly confirmed by Le Bel and van't Hoff. While the mere study of the constitutional formula of a chemical compound permitted one to predict its optical activity and to calculate the number of its isomers, nevertheless it provided no means to foresee the amount, or at least the direction, in which it would turn the plane of the polarized light. Guye's hypothesis of the "asymmetric product" was to fill this gap. His hypothesis attributed the principal rôle in optical activity to the mass of the groups connected with the asymmetric carbon atom. The development of the hypothesis becomes very simple if, in a first approximation, the centers of gravity of the four groups connected with the carbon atom are placed at the corners of a regular tetrahedron. When the masses that are combined with the carbon are not all different, the center of gravity of the molecule is located at least in one of the six planes of symmetry of the regular tetrahedron. If, however, the carbon atom is asymmetric, the center of gravity will be outside of these planes. Designating the distances of the center of gravity from each of the six planes of symmetry in the molecular model by d_1 , d_2 , d_3 , d_4 , d_5 , d_6 , then further arbitrarily counting the distances as positive on one side of the plane, negative on the other, Guye defined the product of asymmetry as

$$P = d_1 \cdot d_2 \cdot d_3 \cdot d_4 \cdot d_5 \cdot d_6.$$

This product should measure the dissymmetry of the tetrahedron and, at the same time, the degree of optical activity.

At first, the hypothesis seemed to be confirmed qualitatively. The sign (positive or negative) of optical rotation changed when a substitution in an optically active molecule displaced the center of

gravity in relation to one of the planes, and the sign remained the same when the center of gravity stayed on the same side of the plane. In his first work on this subject Guye examined over a hundred optically active derivatives in seven different series; they all verified, with a few exceptions, his bold and fruitful hypothesis. These findings caused a great stir and provoked a considerable number of parallel studies.

However, the exceptions to the rule increased in numbers. Guye tried to explain them by assuming that the tetrahedron was deformed through the chemical affinities of the substituent groups, since the masses, instead of being strictly concentrated in the corners of the tetrahedron, are located at distances depending on their molecular volumes.

The other problem which Guye studied at the same time was molecular constitution. In 1890 he found a relationship between the volume b in the equation of van der Waals:

$$\left(p + \frac{a}{v^2}\right) (v - b) = RT$$

the critical coefficient and molecular refraction. This enabled him to determine molecular weights at the critical point (of temperature and pressure, where the difference between gas and liquid disappears) and to state that at that point water and alcohols are polymeric. A series of experiments started from here: measurements of temperatures, pressures, and critical volumes or surface tensions, of theories like the calculation of the constants a and b in the van der Waals equation, and of modified forms of that equation. Guye can rightfully be said to have contributed very essentially to the study of polymerizations in liquids.

In 1900, and for several years thereafter, he undertook experimental studies of the industrial electrolysis of alkali chlorides. This resulted in a publication on the theory of electrolysis using diaphragms. By a simplified calculation he established a whole set of relationships from which the yields of electrolytic operations with diaphragms could be calculated in advance for different schedules. The final confirmations of this elegant theory showed that it can be applied whenever one of the products of an electro-

lytic process becomes an electrolyte itself and thus contributes to the flow of the current.

From 1903 on the investigations on atomic weights, the most important part of Guye's work, described in almost 100 reports and articles, began to be published. He approached this particularly difficult subject in the full bloom of his talent. It is the work of his maturity, and it is hard to decide which to admire most: the magnificent order of the over-all plan he followed during twenty years, the perfection of the technique, or the importance of the results achieved.

The starting point was a divergence in the value for the atomic weight of nitrogen obtained by purely chemical methods and from physicochemical measurements of the density of this gas. By six chemical methods, Jean Servais Stas (1813–1891) had obtained a remarkable agreement for an average figure, namely, 14.044, whereas the physicochemical measurements particularly favored by Guye at that time gave 14.005. Such a difference was not admissible, especially for the fundamentally important atomic weight of nitrogen. Therefore, Guye began to organize research in Geneva to find the necessary corrections. He thought that these corrections should involve simultaneously the chemical methods for establishing the relationship between nitrogen and oxygen more directly than Stas had done and the physicochemical methods. For the latter, precise measurements of densities and compressibilities had first to be carried out with several gases containing nitrogen, then these had to be calculated by means of the new statistics which Guye had applied to deviations from the law of Avogadro. Among these methods of calculation, that called reduction of the critical constants deserves to be especially mentioned; Guye described it in one of the most beautiful of his papers.

It was no easy matter to carry out such a plan, because after all it required improving upon Stas, that great experimenter, and in addition surmounting new difficulties in physicochemical procedures. The successful accomplishment of this program perhaps best characterizes the special gifts of his school.

Guye had often expressed the thought that one can never be absolutely certain that a gas is pure. It could be ascertained only

by preparing the gas under varying conditions from different chemicals and with several methods for purification. Besides, chemical means of purification permit only the removal of known impurities. Therefore the chemically purified gas must always be subjected to a physical purification, either liquefaction and fractional distillation, or fractional freezing. According to the Geneva school, the best criterion of purity for a gas consists in measuring a characteristic property, such as density—needed anyway for the calculation of the atomic weight—which must be found the same for samples of different origins after careful physical purification. This technique was not created in one day; gradually, with necessary improvements, it reached such high perfection that Guye's laboratory became justly famous for it. The measurement of gas densities by the classic method profited from the research at Geneva; through a series of improvements it reached an absolute guaranty of precision of about 1 in 10,000.

Four years of organized teamwork were necessary to demonstrate that the 14.044 value of Stas was inaccurate. In a lecture presented on June 10, 1905, before the Société Chimique de France, which was reproduced in English in 1906 and in German in 1907, Guye formulated the following conclusions: Physico-chemical and direct chemical methods are in as perfect an agreement as possible, the average being 14.008 for the former, 14.009 for the latter. The value which Stas obtained by six indirect methods should, therefore, be abandoned.

However, it was not sufficient to make these statements; it was also necessary to explain how the illustrious Belgian chemist could have been so mistaken. By a painstaking analysis of the experimental procedures Guye showed that, contrary to all expectations, none of the indirect methods of Stas was accurate to the second decimal for the atomic weight of nitrogen, and that the error was ascribable to the atomic weight of silver. According to Guye, this atomic weight should be reduced to 107.89.

These conclusions of the Geneva school were naturally received with attention, but it took no less than nine years before the results of Professor Guye acquired full status. The International Committee for Atomic Weights decided to adopt the new value of

14.01 for nitrogen in 1907 and, two years later, 107.88 for silver. This latter modification was arrived at, following work at Harvard and Geneva.

Side by side with purely scientific studies Guye was creatively active in a quite different direction. He was not actually a technologist, but none of the great industrial questions was alien to him. His name was an introduction to the leaders of industry; his charm made them his friends; his resolute integrity opened factory doors for him that were jealously closed to anyone else.

His name is inseparably connected with the electrochemical synthesis of nitric acid. He had begun the study of this problem in 1893 with Aloys Naville and Charles-Edmond Guye (his brother), then continued it with other collaborators, and in spite of all kinds of difficulties had finally succeeded. The principles embodied in his patents of 1895 also guided subsequent inventors: the cooling of gas, after it has passed the electric arc, by an excess of air, and the contraction of the gas stream between the electrodes.

Guye quickly realized that the problem of nitric acid is not limited to its synthesis. The great use for combined nitrogen is in fertilizers, and the costly product is the concentrated nitric acid. The nitrous gases from the electric ovens permit only the initial recovery of 30 per cent acid. The nitrate of calcium is inconvenient because it is hygroscopic. Guye and his group studied how to convert the chlorides of potassium and sodium into nitrates by means of dilute nitric acid, and they established the practical conditions which avoid forming nitrosyl chloride, the great stumbling block in this reaction. They also contemplated the use of nitric acid to solubilize the phosphates alone or in mixture with potassium salts.

Because of his polite manner and his scientific reputation, Guye exerted great influence on scientific societies, Swiss as well as foreign. Aware of what a journal can accomplish for the development of a science he created the *Journal de chimie physique*, which soon became the medium for physicochemists in all countries who wanted to publish their papers in French. Guye also was instrumental in creating the *Helvetica Chimica Acta*. The success of this journal and its high scientific level justified the ideas of its promoters.

His fruitful and disinterested activity naturally brought him

PHILIPPE-AUGUSTE GUYE

many distinctions. They were numerous and of the highest order. However, Guye placed the affection of his students above these marks of appreciation and these honors; those who write these lines bear moving testimony for this fact. (This article resulted from the collaboration of several former students and friends of professor Philippe-Auguste Guye, and it was edited by one of them.)

From: *J. chim. phys.*, 20, 1 (1923), abbreviated. Translated by
Eduard Farber.

E. BRINER

.. 79 ..

John Ulric Nef

1862-1915



JOHN ULRIC NEF, together with Arthur Michael¹ and Ira Remsen,² was prominent in the establishment of graduate study in the universities of the United States and in the transfer thereto of the science and techniques of organic chemistry from the university laboratories of Europe. Nef was a great experimentalist, an inspiring teacher, and a pioneer in theoretical organic chemistry. His Ph.D. trainees went into many of the American universities, especially in the Midwest, and helped to establish research in organic chemistry at the graduate level in these institutions. Nef was very inspirational and imbued his students with an intense love and devotion for their science.

John Ulrich Nef was born on June 14, 1862, at Herisau, Kanton Ausser Appenzell, Switzerland, as the eldest of two sons of Johann Ulrich Nef (1834–1884) and Anna Katherina Mock Nef (1842–1910). His father was employed as a foreman in one of the textile mills for which that Swiss canton was famous. Being of an adventurous turn of mind, he came to the United States in 1864 to investigate the possibilities of the textile industry here; finding a suitable position as foreman in a textile mill at Housatonic, in southwestern Massachusetts, he brought his family there in 1866 and settled them in a small farmhouse four miles from the town. At this time his son Ulrich, as his mother addressed him, was only four years of age. The son later attended school at Great Barrington and every school day, rain or shine, he would walk the four miles to that town and return again in the afternoon. In addition, he had his regular chores to perform at home. His father was an excellent preceptor and instilled in his son a love of books, music, sports, and work. It was to this early training that the son ascribed his lifelong belief in a balance between strenuous intellectual work and equally strenuous physical exercise, as a foundation for a well-rounded life. He became a strong swimmer and once saved his younger brother from drowning. It was while swimming underwater as a youth that he burst an eardrum and became nearly deaf

in one ear. He loved to walk at a vigorous hiker's pace and in later years he played an excellent game of tennis.

When sixteen years of age, it was settled that he should enter college and after spending two years in a New York City college preparatory school, he entered Harvard University at the age of eighteen with the class of 1884. He had planned to enter medicine but from the time he took his first course in chemistry he was fascinated by the tremendous opportunities for research and discovery presented by this discipline. He must have had a good teacher of chemistry. His start in college was not unusually brilliant and he even encountered some difficulties with German—the Appenzeller Deutsch of his home life being insufficient. His facility in scholarship increased, however, and in his senior year he far outdistanced his fellow students in chemistry and received as a reward the Kirkland Traveling Fellowship which enabled him to study further in Europe. His expenses at Harvard had been largely met by summer employment in the textile mills. While in Boston he attended concerts regularly and developed an interest in music and the fine arts which he maintained throughout his life.

John Ulric Nef left for Europe in the summer of 1884, accompanied by his father, who had unfortunately contracted tuberculosis. They spent a summer together in the beautiful region of the Vierwaldstätter See and then his father returned to America where a few months later he died at the age of fifty. Arriving in Munich, where he had elected to study with Professor Adolf von Baeyer³ at the University of Munich, young Nef threw himself into his work and into the cultural life of that German city at its greatest period. After only two years of study he received the Ph.D. *summa cum laude*, in 1886, at the age of twenty-four, with a thesis entitled "Über Benzochinoncarbonsäuren," and concerned with some aspects of tautomerism, a phenomenon which had been discovered earlier by Baeyer in the isatin series. Geheimrat Baeyer was very fond of this intense young man and stated, as reported by Richard Willstätter, that Nef was the most brilliant of all the students he had during his long tenure of the chair of chemistry at Munich. After receiving his degree, Nef continued working in the Baeyer laboratory for an additional year.

In 1887 Nef accepted an appointment at Purdue University, Lafayette, Indiana, at a salary of \$1200, payable quarterly. In making this offer, President Smart wrote as follows: "We have a laboratory at Purdue University in which are 48 individual desks with closets, drawers and individual reagents each. We have room for 16 desks more. The amount of time a man will have for private research will depend on his power of organization. He will be occupied in class and laboratory work about 4 hours a day."

John Ulric Nef demonstrated the "power of organization" required and plunged into an intense period of research activity. The lights of his laboratory burned far into the night. He had no assistance; all the work was done with his own hands. He continued the work begun with Baeyer and published several papers in the *American Chemical Journal* of Ira Remsen, one of which was republished in German in Liebig's *Annalen*.

Nef spent the summer of 1889 in Switzerland. He became much interested in mountain climbing and made many difficult ascents. He loved the mountains and spent numerous summer vacations (every one from 1891 to 1897) in the Alps.

A new American university was opening in Worcester, Massachusetts, under the presidency of G. Stanley Hall and with Jonas Gilman Clark as the benefactor. It was to be operated as a graduate school and opened its doors on September 1, 1889, with John Ulric Nef as assistant professor of chemistry at a salary of \$2,000 a year. A new laboratory was to be built. Following the resignation of Professor Arthur Michael, Nef was named, in April, 1892, director of the Chemical Laboratory. He brought his mother to Worcester but her mind began to fail badly and in 1891 he took her to Switzerland where she was placed in a Protestant sanatorium near Herisau and where she died in 1910. Her son visited her there frequently in the academic summer vacations.

At Clark, Nef worked on the structure of the salts of β -keto acids and of nitroparaffins, and he initiated his researches on bivalent carbon compounds, especially the isocyanides and the fulminates. All was not well with the new university, however. Promised funds did not materialize and in 1892 eight important faculty members resigned. These included J. U. Nef, associate profes-

sor of chemistry, A. A. Michelson,⁴ professor of physics, and Franz Boas,⁵ docent in anthropology. But for Nef, a new position was forthcoming. In the rapidly developing United States of America, another university was beginning and this one had an assured financial backing.

On October 1, 1892, the University of Chicago opened with funds donated by John D. Rockefeller, who gave to it \$37,708,000 during the period 1890 to 1910. William Rainey Harper was its president. Born in a log cabin in Muskingum, Ohio, Harper was that variety of the human species, always rare on the American scene and now essentially extinct, that could be termed a great university president. With the Rockefeller donations, he gathered together a great faculty and even included in it nine former presidents of colleges and universities. The professorship in chemistry was given to John Ulric Nef and he began October 1, 1892, under a contract designating a salary of \$3000, payable monthly, and including a private research assistant. He had insisted upon the latter. Here he remained for the rest of his life. He was named to the head professorship of the department in 1896. Later on, Nef turned over the administrative detail of the department to Dr. Julius Stieglitz while retaining a firm rein on all matters of policy. Stieglitz had been "hired" by Nef in 1892 as a docent. The German university rank of docent, carrying little honor and no pay, never became popular in the States.

Nef was temperamental and impulsive. In 1894 President Harper felt constrained to write him as follows: "Your letter of April 6th has been received. I am not willing that you should carry out the plan which you indicate in it, and I hope that you will not do anything rash."

In establishing graduate work in chemistry at Chicago, Nef had written in 1892 to his friend Professor C. Loring Jackson at Harvard and had been advised that an applicant for the Ph.D. at Harvard must have had either Latin or Greek, preferably both. Indeed, Ira Remsen has stated that he wrote his Ph.D. dissertation in 1870 at Göttingen in Latin. This emphasis upon the classics was not maintained in the science departments at the new University of Chicago.

The task of instructing large classes of undergraduates in a science in which most of them showed little interest was always irksome to Nef but in Alexander Smith⁶ he selected a great teacher of freshman students. The department was housed first in a city flat, but in 1896 it was moved to the fine Kent Chemical Laboratory.

John Ulric had stated that "a scientist should be married to his science." Nevertheless, he married in 1898, at the age of thirty-six, and found in Louise Bates Comstock, of Rochester, N. Y., an understanding helpmate. She was a highly cultivated young woman who had spent five or six years of study and travel in Europe and, as one of Nef's graduate students, she understood and appreciated the rigorous demands of his profession. The summer of 1898 was spent by the young couple in European travel. Their marriage was a happy one but was not destined to endure, for in 1909 Louise Nef contracted pneumonia and died after a very short illness. This was a great blow to Dr. Nef. One son, John Ulric Nef, Jr., survived this union. This member of the third generation bearing this name is a distinguished historian and is likewise a professor at the University of Chicago, where he was the principal founder of the Committee on Social Thought, of which he is the chairman.

In 1903, Dr. Nef suffered a severe nervous breakdown caused by intense overwork and in 1911 he experienced another. He had planned to spend the summer of 1915 in a leisurely trip through the Canadian Rockies, accompanied by his young son, then a lad of sixteen years. Nef's mountaineering was not restricted to the Alps. The greater part of the summer of 1908 had been spent in Estes Park, Colorado, where he had astonished the natives by hiking alone from Elkhorn Lodge to the summit of Long's Peak and back in a single day. His Swiss friends had commented: "Er könnte nicht laufen, er müsste immer springen" (he could not walk, he must always spring). On his 1915 walking trip in the Canadian Northwest, begun in June, he found himself in poor health and hurried to San Francisco at the end of July. There a medical examination showed him to be suffering from acute dilatation of the heart; although his health was not considered to be at all critical, he died suddenly, at the early age of fifty-three, while visiting one of his former students, Dr. Herman A. Spoehr, at the

Coastal Laboratory of the Carnegie Institution located at beautiful Carmel-by-the-Sea in California:

The late Professor William Lloyd Evans, a Nef student, has described Professor Nef as follows:

Nef was rather small of stature with a massive brow, and bright, penetrating eyes. He had an all-consuming and contagious love for his science. One became fascinated with the rapidity of his thought which so out-distanced even the marvelous speed of his words that his students could only take sketchy notes which they would later piece out and amplify in order to get the full value of his lecture. His eager restless enthusiasm for the problems in which he was engrossed, developed in him an appearance of brusqueness which amounted almost to impatience when the research did not progress smoothly. Back of this intellectual eagerness, however, dwelt kindly human qualities. He was by temperament intense and found his relaxation in long walks which he pursued at an unaccompanied speed. He loved music and was a weekly attendant during the season of the Chicago Symphony Orchestra.

Nef was a member of the American Chemical Society, Deutsche chemische Gesellschaft (1885), American Association for the Advancement of Science (secretary, Section C, 1893), Chicago Academy of Sciences (1893), National Institute of Social Sciences, New York (1914), American Academy of Arts and Sciences (1891), Royal Society of Sciences in Upsala (1903), and the National Academy of Sciences (1904). He was awarded the honorary LL.D degree by the University of Pittsburgh in 1915.

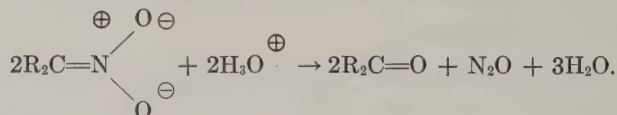
Nef was a highly individualistic worker. Save for three early articles (1884-87) and his last (1917) posthumous one, Nef never published with a co-worker. Even his Ph.D. dissertation with Baeyer appeared with his name as sole author. He straddled, as it were, both sides of the Atlantic and published in the German chemical literature, largely Liebig's *Annalen*. The work of his Ph.D. students appeared independently, mainly in the American chemical literature. His own personal work, carried out with one postdoctoral research assistant, was published under his own name in 34 articles running to some over 1500 printed pages. Although he was fluent in German, it was his custom to send his articles in

that language to his friend Johannes Thiele⁷ for full conversion to the idiom. In 1899, the *Annalen's* editor, Volhard, wrote to Nef: "Ihre schönen Arbeiten erachte ich für eine Zierde der *Annalen*" (I consider your fine manuscript [concerning phenylacetylene] an adornment for the *Annalen*).

Nef prepared a large number of compounds which he described with extraordinary care and precision. He reflected his training with Baeyer in laying great stress on careful manipulation, was most particular regarding cleanliness and orderly assembly of apparatus, and worked as quantitatively as possible. He believed in simple apparatus and in not doing too much at once. He kept a file of research samples. The personality of Nef was so overwhelming that he imparted these traits to his students in no uncertain fashion. Wherever they were, Nef students maintained a clear desk and kept their laboratories scrupulously neat. The story is told of the wrath visited upon a luckless graduate student when Dr. Nef entered the laboratory and spied a burnt match on the floor, and of the time when the doctor, while watching a reaction which at last went out-of-hand, backed away from the apparatus and fell over a stool which should not have been at that spot in the laboratory. Drs. Oscar Hedenburg and J. W. E. Glattfeld were his last personal (postdoctoral) assistants at Chicago and although Nef was in poor health at the time and was doing little or no personal laboratory work, he told them exactly what to do and kept all notebook records himself.

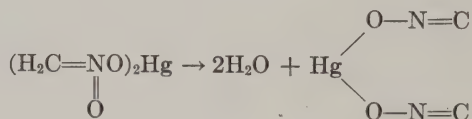
Nef's first independent work, published from Purdue, was concerned with an extension of his work with Baeyer on derivatives of *p*-benzoquinone. At the time he initiated this work, which was mainly concerned with the tetrahalogen derivatives, there were three formulas in vogue for the parent substance. Of the three, the currently accepted one, originally proposed, but not established, by Fittig, was put on a sound experimental basis by Nef. On moving to Clark, he turned his attention to the sodium salts of β -ketonic esters for which he favored the enolic formula. In common with many organic chemists of the time, he did not like shifting tautomeric structures, stating that: "To explain the behavior of an organic compound one formula is sufficient." From the sodium salts of β -ketonic esters he proceeded logically to a study of similar

salts of primary and secondary nitroalkanes. He showed that acids did not regenerate the nitroalkane but gave a carbonyl compound. In modern terms,



This is known as the Nef reaction—one, however, of several “Nef reactions.”

In order to study the various salts of nitromethane, it became desirable to prepare the mercuric salt which had been reported to be an explosive, yellow solid. In preparing this dangerous substance, Nef noted that the warm liquid filtered from it gradually deposited crystals which he recognized as the fulminate of mercury. This chance observation was utilized by Nef to establish the true formulas of the fulminates, which had hitherto been considered, following Liebig and Gay-Lussac, to be salts of a dibasic acid. Nef formulated the reaction as follows:



He recognized the bivalency of the carbon atom in fulminic acid, isolable only as its salts. In conclusive proof of this, he isolated the carbon hydrohalide addition compound, $\text{HON}=\text{CHCl}$. This compound, extremely poisonous, crystallized from ether at 0° in long, transparent needles which turned green on warming to room temperature and exploded with violence. In a search for other bivalent carbon compounds, he studied prussic acid, its salts, and the alkyl isocyanides. He favored the formula $\text{H}-\text{N}=\text{C}$ for prussic acid. He was greatly interested in the peculiar compounds $(2\text{RNC}) \cdot 3\text{HCl}$ and in those obtained from metallic cyanides by the action of alkyl hypochlorites.

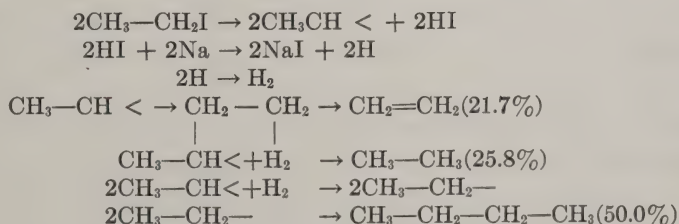
In later work he was intrigued with that most unsaturated of carbon compounds, acetylene. He prepared and studied its halogen substitution products, all poisonous and spontaneously combustible

compounds. Diiodoacetylene possesses an odor deceptively like the isocyanides and dissociates explosively at 100° into its elements. Nef formulated it, probably incorrectly as $\text{I}_2\text{C}=\text{C}$. In connection with his studies on acetylene, Nef established the ethynylation of a ketone, a reaction which has been exploited in recent times and which constitutes a key step in the modern, commercial synthesis of vitamin A,



The above is the "Nef reaction" of the acetylene chemist and is not to be confused with the "Nef reaction" of the nitroparaffin chemist.

All this difficult and dangerous experimentation set Nef to speculating on the nature of the valency of carbon. Recognizing explicitly that the nature of valence was at the time unknown, he began by attacking the Kekulé concept of the constancy of the tetravalency of carbon. He considered that carbon, like other reactive elements, should have several valence states, in this case two and four. This was an entirely logical assumption. He then exploited the ascribed tendency of carbon to react in these two valence states as a general phenomenon in the reactivity of carbon compounds. His theory of methylene dissociation postulated that a carbon compound, like an alkyl halide, first dissociated into a reactive bivalent carbon radical which then could react in various ways. He explained the Wurtz reaction as follows, the product yields being those established by him:

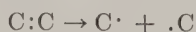


Nef hoped that his methylene dissociation theory would serve organic chemistry as the Arrhenius ionic dissociation theory served inorganic chemistry. The theory was a logical one for the time and

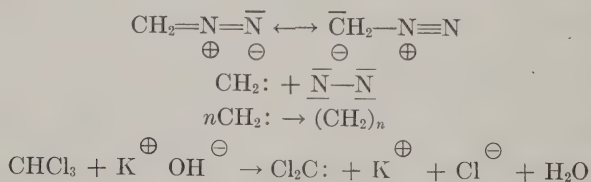
contained germs of truth which served to stimulate further work.

Our modern theory of the transition state is foreshadowed in the words of Nef (*italics mine*): "Excluding all reactions called ionic, a chemical reaction between two substances always takes place by their union to form an addition product. The one molecule being unsaturated and partially in an *active molecular condition*, absorbs the second molecule. The resulting addition product often dissociates spontaneously giving two molecules."

With the later establishment of the covalent electronic bond, the modern radical theory evolved from the concept of its homolytic splitting followed by recombination and further reactions of the dissociated products:



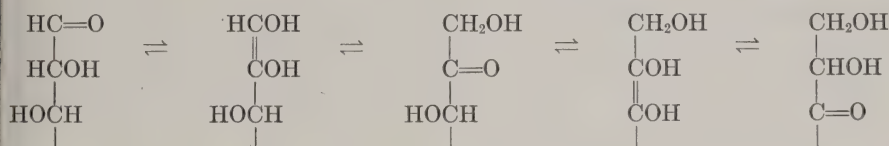
These radicals are not of necessity bivalent although such are known, as in diazomethane decomposition (Nef's long-sought methylene) and in the alkaline haloform reactions:



These speculations, with much experimental data offered in their support, were published in four long articles in Liebig's *Annalen*. The fourth appeared (1897) in an article of 172 pages length. These pages were for many years the most thoroughly thumbed of any of the journals in the Kent library and were considered to be "required reading" by all the Nef students at Chicago. An important point to be derived from them is the emphasis placed by Nef upon *all* the products of a reaction and not just the one desired end-product. To Nef by-products were as important as the main product in delineating the true nature of the reaction under study. In this respect he did not overlook polymerization. In 1904 he wrote: "Experience has shown that many unsaturated compounds can not be isolated; but polymerize spontaneously. It is clear that when the per cent of active particles present in an un-

saturated compound becomes relatively great the possibility of their uniting with each other to form condensed molecules increases." Here, indeed, is a true conception of our present theory of polymerization which had to be laboriously rediscovered by others many years later.

During the last period (1904–1915) of his relatively short life, Nef and his students at Chicago devoted their entire attention to a comprehensive study of the dissociation of the sugars in alkali and when under oxidation in neutral, acid, and alkaline media. The results were published in three long articles of 98, 118, and 179 pages, respectively, in the *Annalen*, appearing at intervals of three years.⁸ The experimentation was designed in the hope that some light might be thrown on the fermentation of sugars. In this extensive and difficult work, Nef and his students separated the saccharinic acids (alkali rearrangement products of the sugars) and established the structures of their various types. He established the concept of the intermediate enediol and its movement along the carbon chain:



He studied chain degradation and especially lactic acid formation by alkali. With Oscar Hedenburg, he discovered the second and highly unstable form (1,5) of the aldonolactones. He obtained the next lower aldose by rapid air oxidation of an alkaline solution of an aldonic acid, which constitutes the "Nef reaction" of the sugar chemist and represents the third "name reaction" ascribed to him.

Nef's untimely death in 1915, at the age of fifty-three, brought his personal researches to an abrupt end, but they were continued by his students. During his last period at Chicago he trained most of his major students who, imbued with the intense research spirit imparted by Nef, continued thereafter in carbohydrate research, with their own students, in universities and research institutes located mainly in the Midwest. There can be cited the names of

Ernest Anderson (Arizona), William Lloyd Evans (Ohio State), J. W. E. Glattfeld (Chicago), Oscar Hedenburg (Mellon Institute), W. Lee Lewis (Northwestern), Herman A. Spoehr (Carnegie Institution), and Fred W. Upson (Nebraska). Among earlier students at Chicago were S. F. Acree (National Bureau of Standards), Lauder W. Jones (Princeton), and William McPherson (Ohio State). Considering that Nef only had 25 Ph.D students at Chicago, this is a very high percentage (40 per cent) of students who later made their mark in fundamental research activities. The great personality of Nef was impressed upon these students, and all of them respected and revered their master.

Nef and his school were interested in the chemical reactivity of carbon compounds and were never interested in synthesis alone, although organic synthesis was the main theme of their American contemporaries. None of his immediate students would have known what were meant by the "Nef reactions" now so well-established in that vast collection of "name" reactions of the modern organic chemist. His work foreshadowed the modern theory of the transition state, and of organic radicals and their polymerization. The contributions of Nef and his school to theoretical and synthetic chemistry were profound and timely, and his influence on the development of organic chemical research, especially in the United States, has been immeasurable.

GENERAL REFERENCES

- F. Henrich, T. B. Johnson and Dorothy A. Hahn, "The Theoretical Speculations of John Ulric Nef" in *Theories of Organic Chemistry*, John Wiley, New York, 1922, pp. 334-60.
- L. W. Jones, "John Ulric Nef," *Proc. Am. Chem. Soc.*, 44-72 (1917).
- J. U. Nef, "On the Fundamental Conceptions Underlying the Chemistry of the Element Carbon," *J. Am. Chem. Soc.*, 26, 1549-77 (1904).
- M. L. Wolfrom, "John Ulric Nef," *Biographical Memoirs*, National Academy of Sciences, U.S.A., XXXIV (1960), pp. 204-227.

NOTES AND REFERENCES

- 1 Arthur Michael (1853-1942). Born in Buffalo, New York; studied in Germany and France from 1872 to 1879; professor of chemistry at Tufts College, 1881-1890 and 1894-1907; professor of organic chemistry at Harvard, 1912-1936.

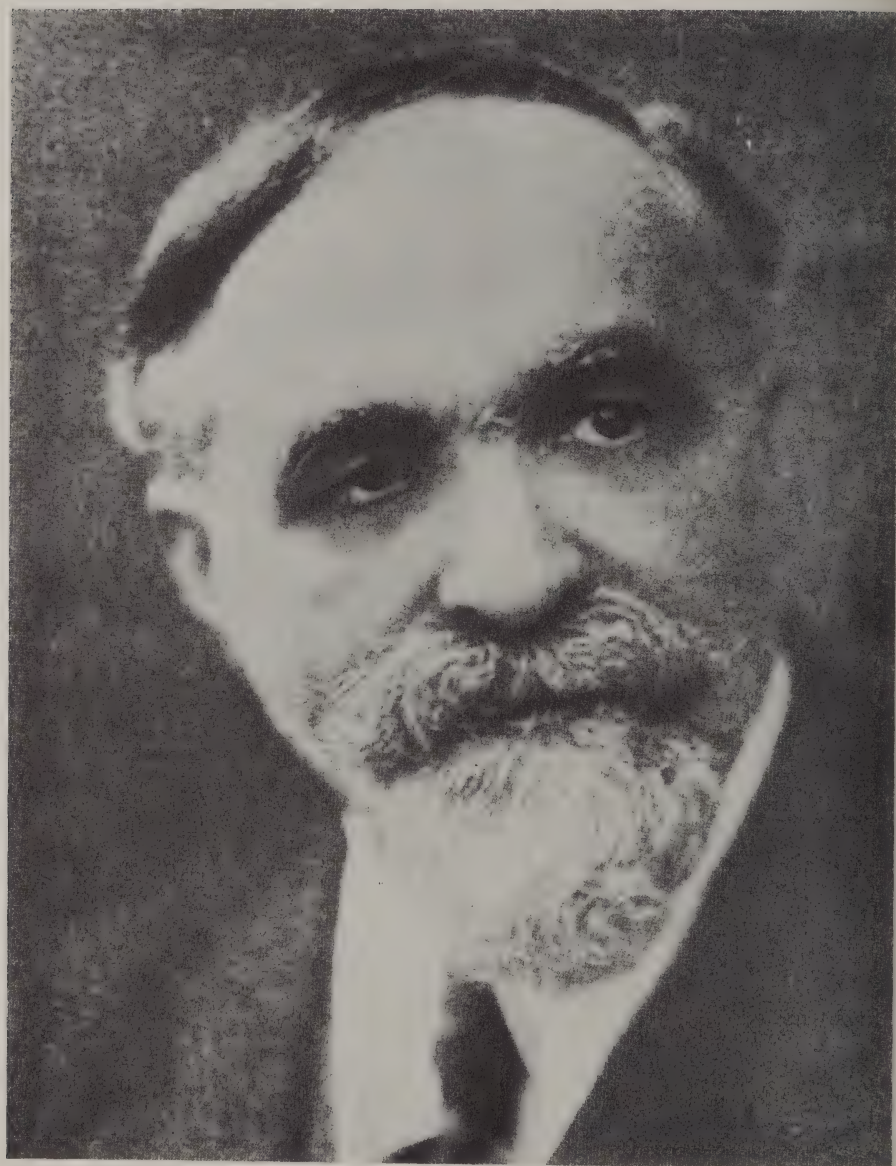
- 2 Ira Remsen (1846–1927). Born in New York City, he was educated at the College of the City of New York, Columbia (M.D.), and Göttingen (Ph.D.). He was professor of chemistry at Johns Hopkins University from 1876 and president there from 1901 to 1912.
- 3 *Das Buch der Grossen Chemiker*, Band II, G. Bugge, editor, Verlag Chemie, Berlin, 1930, p. 321 ff.
- 4 Albert A. Michelson (1852–1931), physicist and first American Nobel laureate, renowned for his accurate measurement of the velocity of light, went with Nef to the University of Chicago.
- 5 Franz Boas (1858–1942). Renowned anthropologist. Born and educated in Germany. Professor at Columbia University and associated with the American Museum of Natural History in New York City.
- 6 Alexander Smith (1865–1925). Born in Edinburgh; Ph.D. from Munich in 1889. Professor of chemistry at Wabash College, Indiana (1890–1894), Chicago (1894–1911), and Columbia (chairman, 1911).
- 7 Johannes Thiele (1865–1918). Pupil of Volhard and his successor (1910) as editor of the *Annalen*. Professor of chemistry at Strasbourg.
- 8 In the Sharp Chemistry Library of The Ohio State University, these articles have been so thoroughly thumbed that all three volumes of these *Annalen* have had to be rebound.

MELVILLE L. WOLFROM

.. 80 ..

Charles Moureu

1863-1929



LIFE

ON JUNE 13, 1929, François-Charles-Léon Moureu passed away at Biarritz. He was a member of the Institut and of the Académie de Médecine, professor at the Collège de France, and Grand Officier of the Légion d'Honneur. This event plunged French science into widespread mourning, affecting particularly the Société Chimique de France, because in its former president it lost the person who had promoted its prosperity and its luster.

Charles Moureu was born on April 19, 1863, at Moureux, a small village in the Bearn country. He was the last of seven children in a rather poor farmer's family. Nothing in his humble origin, in the rustic house of his parents, or in the misfortune of losing his father very shortly after his birth indicated the brilliant future lying in store for him.

His education started in the grade school of the village. This beginning of his intellectual formation left an indelible impression, and he always felt deeply grateful to his old teacher. With remarkable intuition his mother believed that this flowering intelligence had great promise, and without regard to the heavy burden of educating her six other children she did not draw back from the additional sacrifices which the further education of her son Charles would necessarily involve.

In the period beginning with his college career his biography cannot be separated from that of his brother Félix. After obtaining the diploma of a pharmacist, Félix had opened an apothecary shop at Biarritz which soon prospered. This circumstance became a decisive influence in the career of Charles. The brother, replacing the lost father, became banker, guide, and friend at the same time. It was he who oriented the student toward pharmaceutical studies and, thereby, toward a scientific life.

In November, 1884, Moureu entered the École Supérieure de Pharmacie at Paris. He soon distinguished himself by earning the principal awards in the competitions held for the most gifted of the students.

After that, it was an uninterrupted series of successes. As an

intern in the hospitals of Paris he gained successively the silver medal (1887) and the gold medal (1889). In 1891 he won the title of chief pharmacist of the Asiles de la Seine. At the same time, he conquered several academic grades: Licencié ès sciences physiques in 1888, pharmacist of first class in 1891, doctor of toxicology in the École Supérieure de Pharmacie de Paris in 1899. From this listing one may judge how much hard work occupied the life of this student. In his eyes, however, this was only an accessory. The main thing that took hold of his spirit and his time was an irresistible inclination, an ardent passion for science and, especially, for chemistry.

At that time, he had the good fortune of meeting, in the family of Bertrand Louber, the wonderful companion of his life who understood and helped him and joyfully shared with him the austere existence of a scholar. From now on, nothing stood in his way; he was able to satisfy his aspirations and to give free rein to his creative abilities.

He did not have to wait long for results. His doctor's thesis, dealing with the difficult subject of acrylic acid and its derivatives, had demonstrated a real experimental skill and an inventive mind. Shortly afterward his publications started to multiply while the fields of his investigations and the importance of his discoveries expanded. The originality of the researcher and his activity quickly attracted attention. Encouragements, rewards, official recognitions, and finally the highest titles followed upon one another with incredible speed.

Success, instead of blunting his zeal, exalted it; if he had worked without truce before, he now worked with redoubled effort. However, this intensive productivity was not of long duration; World War I interfered.

It was a critical moment; it was necessary to win or else be subjugated. In the unity of general patriotism, the French chemists went to work. This scientific mobilization, its protagonists, its secret labor, its results, all this has been magnificently described by Moureu in his book: "*La Chimie et la Guerre. Science et Avenir*" (*Chemistry and the War. Science and the Future*, Paris, 1921).

The end of the great drama did not open up an era of calm immediately. Less than anyone else Moureu was inclined to let

things slide; a new phase of his life began. The material and moral ruin to which he was a wounded witness released his energy. He saw in science the source of abundance which would permit recovery. He devoted himself to chemistry with increased and improved facilities as successor to Berthelot's chair at the Collège de France to which he was elected in 1917. However, since the events of the war had elevated him to the summit of the general interest, he no longer remained encircled by the limited horizon of his own research. All of science became his concern, because its many branches form a unity. He campaigned energetically to save our several scientific organizations by attracting devoted persons and resources.

He became a master in negotiations to achieve the annual reunion of the world's great chemical organizations. The resultant International Union of Pure and Applied Chemistry asked him unanimously to become its first president. He contributed to the dignified union between the scientists of the two parties formerly at war, a work in the interest of peace which he steered between the dangers of ill advised dissoluteness and too opinionated rancor.

This is, in bold outline, the life of Moureu after the afflictions of the war until the day when his strength, spent in the service of so many generous causes, finally abandoned him.

The death of his brother Félix in 1928 gave him a shock from which he could not recover. Nevertheless he made an effort to attend the Congress at Cambridge in September, 1928. The following winter his health was bad and his strength continued to decline. His doctors, alarmed with good reason, advised a sojourn in the south, at Cambo. This sojourn at Cambo soon became unbearable to him. He went on to Biarritz where, a few days later, death overcame him at the age of sixty-six.

Moureu had a strong personality which emanated a captivating charm. In his manners as in his thought or language, he was an enemy of vulgarity and always gave a high impression of the refinement of the scientist. He gave himself entirely to his teaching, either by lecture or in writing. His nature did not permit him to do anything incompletely, and his biography could almost be condensed into one word: enthusiasm.

BOOKS

Charles Moureu's considerable work, in its variety, is evidence of his indefatigable activity.

The most important of his books was the "Notions fondamentales de Chimie organique" (1st ed., 1902, English translation of the 6th ed. with the title: "Fundamental Principles of Organic Chemistry," by W. T. K. Braunholz, 1921).

Another book that had a resounding success was "La Chimie et la Guerre." The first purely technical part is a kind of inventory of the applications which chemistry found among the belligerents. In the second part the author takes a broad view and issues severe warnings with calm impartiality. Certain pages of magnificent flight of the imagination are veritable hymns to the beauty of science.

Moureu was first of all an organic chemist. Nevertheless his scientific curiosity incited him to start other studies in which he soon became master; it was he in particular who introduced the systematic study of the rare gases in France. Moureu thought that the gases contained in thermal springs should reveal by their composition useful information about the mysterious origin of these waters and their therapeutic action. The previous analyses had given all that could be expected about the known gases; now it was desirable to investigate the new rare gases. This was the start for work on hydrology and the physics of the Earth.

ACROLEIN AND ACRYLIC ACID

Acrylic acid, $\text{CH}_2=\text{CH}-\text{COOH}$, the first of the acids with an ethylene group, was very incompletely known in 1890, when Moureu began its study for his doctor's thesis. His process for obtaining this acid, later elaborated still further with his student Chaux, consisted in oxidizing the corresponding aldehyde, acrolein $\text{CH}_2=\text{CH}-\text{CHO}$ in an indirect way. It was first converted, by addition of hydrochloric acid, into $\text{CH}_2\text{Cl}-\text{CH}_2-\text{CHO}$, or rather its trimeric compound, which was then oxidized. The β -chloropropionic acid, $\text{CH}_2\text{Cl}-\text{CH}_2-\text{COOH}$, thus obtained was transformed into the unsaturated acid through elimination of HCl .

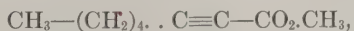
This method made acrylic acid accessible and permitted the

preparation of a new series of derivatives, such as the anhydride, the chloride, the amines, the nitrile, and several esters. All these substances are remarkable for their tendency to polymerize; most of them resinify more or less rapidly.

Moureu returned to these studies because of the war. His first contacts with acrolein had left with him the impression that this was a dangerous material. He proposed its use as a war gas and had it accepted as such when he succeeded, together with Lepape, in obtaining it in stabilized form. The process consisted in conducting the classical preparation (reaction of acid potassium sulfate with glycerin) with certain precautions which were found effective in leaving stabilizing impurities in the product. The nature of these favorable impurities is unknown, but a systematic study, in which Dufraisse, Pougnet, and P. Robin participated, led to the finding of phenol and from there to the discovery of the stabilizing action of phenols. Later, as will be described further on, this stabilizing action was demonstrated as due to an anti-oxygen effect.

ACETYLENIC COMPOUNDS

Moureu successfully developed practical methods for obtaining substances which contained the triple carbon bond together with others of the chemically active groups. This resulted in a long series of new substances, some of which aroused great interest, as for example the *heptinocarbonate de methyl*,



a perfume better known under the name *vert de violette*, and the acetylene dinitrile, $\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, or carbon subnitride.

On the other hand, the knowledge of the acetylenic bond was enriched by his studies which showed the extraordinary reactivity of this carbon linkage.

CHEMICAL CONSTITUTION OF SPARTEINE

In collaboration with A. Valeur, Moureu undertook a study of long duration to find the constitution of a natural product, sparteine, an alkaloid of the furze plant. This important work is a

phenols, "orca" does not resemble the bakelite resins either in the conditions of its formation or in its properties. It is characterized by two main properties which distinguish it from similar resins; it is transparent and a very good electric insulator. It is so transparent that even in a thickness of one meter it looks "optically clear." Together with its optical dispersion, this property might be useful in optics. As an electrical insulator it surpasses all known materials except amber.²

CATALYSIS OF AUTOXIDATION ANTIOXIDANTS AND OXIDANTS

From all the observations on acrolein, Moureu and Dufraisse theorized that the phenols hindered the absorption of free oxygen by acrolein. Thus started the idea of an experiment which seemed strange, if not absurd, at that time. The idea was that an oxygen-absorbing substance (acrolein) should be combined with another substance which itself avidly attracts oxygen (a polyphenol), because such a combination of two appetites would arrest the consumption of oxygen instead of increasing it. This was actually found to be true, as stated October 21, 1917, and later confirmed for a large number of substances; this was the "action antioxygène," antioxidant action.

New as they were, these experiments were not the first to show an antioxygen effect; other very interesting observations had been made before.³ The best known of these was the extinction of phosphorus in air by diverse vapors.

For a systematic exploration, Moureu organized a large program at the organic laboratory of the Collège de France. A great number of catalysts were prepared, all of them painstakingly purified to avoid errors due to impurities. A multitude of measurements of the rate of oxygen absorption was needed, since each catalyst was tried with several autoxidizable substances, often at various concentrations. Each experiment was rigorously controlled, and so were the calculations and the graphs, and arrangements were made to permit later checks on all the data. The collaborators in this long and difficult work were Badoche, Berchet, Chaux, Johnson, Laplague, Lotte, and Panier des Touches.

The following survey of March, 1929, gives an impression of the size of the experiments. At that time, 529 catalysts, inorganic or organic substances, had been tried with more than 30 synthetic or natural materials. The 88,500 measurements of oxygen absorption had served to construct 5100 graphs. To this was added a bibliography comprising over 10,000 documents.

Thus the true nature of the antioxygenic phenomenon could be established with certainty. This phenomenon consists in a kind of paralysis of the oxygen which seems to have lost its reactivity. The gas rests, as if inert, in contact with the autoxidizable substance which is provided with a protective substance, and at the end of the experiment both substances are recovered in their original state of purity without alteration; this really is an antioxygenic effect. The results can be condensed into the following twin propositions: (1) Every autoxidation must be preventable by an appropriate antioxidant, and (2) every chemically reactive substance must be able to function as an antioxidant under the proper conditions.

In view of the importance of autoxidations on the surface of the Earth, the antioxygenic action in its generality must be regarded as one of the great phenomena in nature. In order to emphasize its significance while honoring our departed master, the famous English chemist, H. E. Armstrong, designated this phenomenon as "the Moureu effect."

Another great result was the recognition of the inverse catalyses. This means the property of one and the same catalyst to be able either to promote or to prevent autoxidations, in other words, to function at times as a pro-oxidant, at others as an antioxidant.

This relatedness of the inverse catalyses must not be forgotten in the practice of the antioxidants, otherwise there may be great trouble. An apparently insignificant change in the composition of the catalyst, or in the conditions of its use, may actually reverse the direction of the catalysis. The result is then the opposite of what was hoped for, because the action of oxygen is speeded up instead of being slowed down.

Although relatively young, antioxidants have already begun to find numerous useful applications. Several biological conclusions,

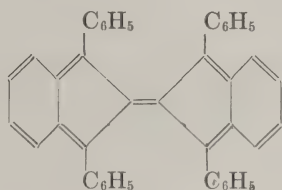
published in 1922,⁴ have been experimentally tested and may lead to applications, particularly in medicine.

Ahead of biology, industry widely uses the data on antioxidants and pro-oxidants. The example of fuels for internal combustion in motors is typical. But of all the industries, that of rubber is the most advanced in putting antioxidants to work.

RUBRENE

Rubrene is a hydrocarbon, $C_{42}H_{28}$ which Moureu and Dufraisse discovered.

This was the last study that Moureu undertook, starting in 1926. Its constitutional formula is



It is an orange-red crystallized substance which gives solutions of rose color and yellow-green fluorescence. These solutions are stable in the dark or, with exclusion of air, under light, but they are rapidly discolored by irradiation in the presence of air. The product of oxidation, called oxyrubrene, is formed by the addition of one molecule of oxygen to one of rubrene; its formula, with R representing rubrene, is RO_2 (with solvent inclusion when the substance is crystallized). Under the action of heat or light, it dissociates into rubrene and free oxygen, $R + O_2$.

This property of rubrene to form an addition product with oxygen which dissociates and regenerates the absorbed oxygen has been called reversible oxidability. This would be unique among organic compounds if there were not another example, and a really capital one, the example of the respiratory pigments of the animals, of which hemoglobin is the representative. Up to now most of the authors placed the reversible oxidability of hemoglobin on the atom of iron it contains. After the example of rubrene, the essential function of hemoglobin can no longer be considered as

necessarily located in the atom of iron; it may, certainly, be connected with this atom, but it can also belong to an atomic group around the iron, or to a group without iron.

Oxyrubrene, $R(O_2)$, corresponds quite well with the intermediary peroxide, symbolized as $A(O_2)$, which is postulated in the theory of the antioxidants. On the other hand, the rubrene problem, which touches on the mechanism of autoxidation in living organisms, has been highly illuminated by the research on catalysis in autoxidation. The fundamental phenomenon of oxidation through free oxygen is thus approached in its widest generality, and the studies of Moureu's laboratory have brought apparently divergent experiences together toward the solution of a great scientific problem.

NOTES AND REFERENCES

James F. Norris, "Charles Moureu," *J. Am. Chem. Soc.*, 52, 31 (1930).

1 Robert Robinson, "The Structural Relations of Natural Products," Oxford University Press, London, 1955, p. 74.

2 *J. Phys.*, 5, 161 (1924).

3 *Chem. Rev.*, 3, 113 (1926).

4 *Compt. rend.* 174, 258 (1922).

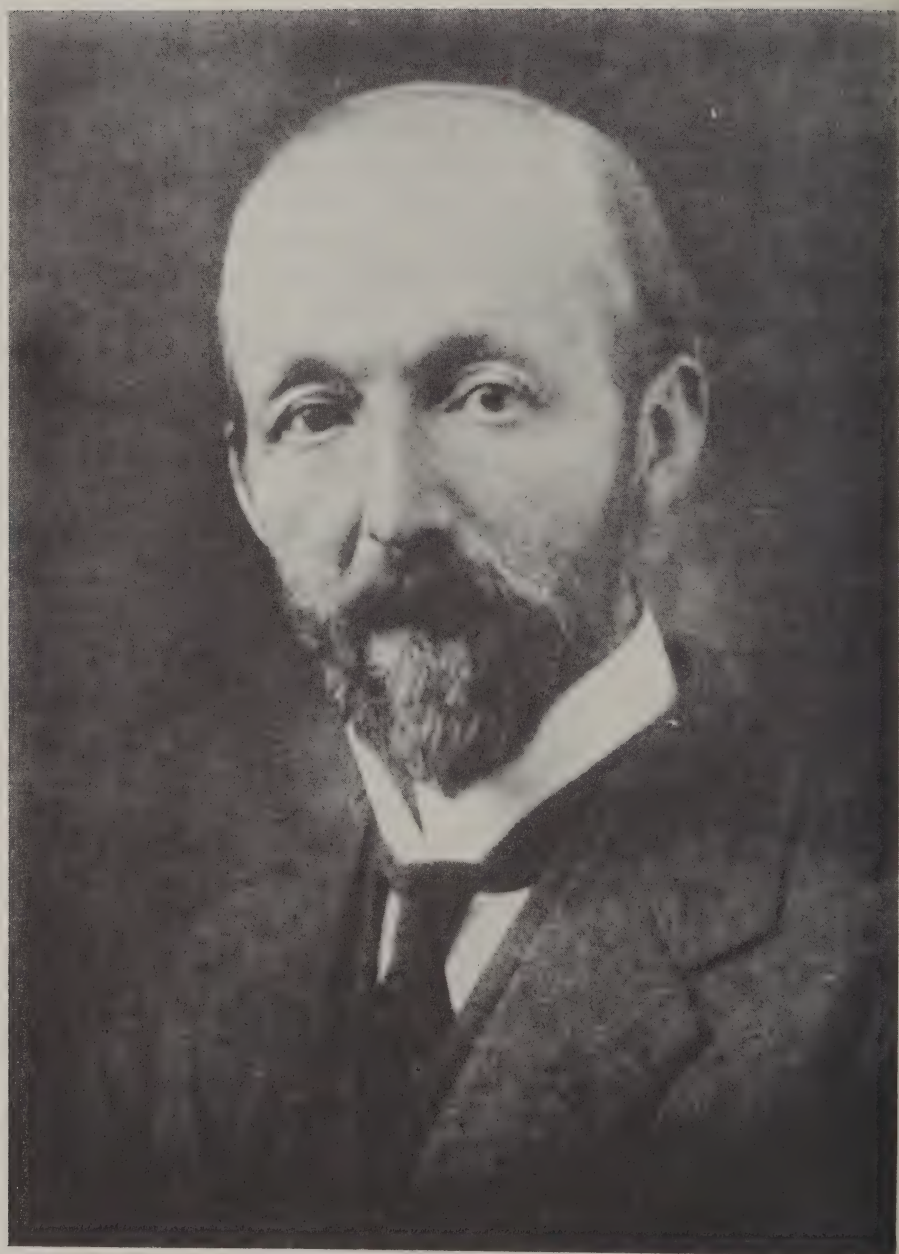
Selections from the biography by Charles Dufraisse, *Bull. Soc. chim. France*, 49, 741 (1931). Translated by Eduard Farber.

CHARLES DUFRAISSE

.. 81 ..

Frederic Stanley Kipping

1863-1949



FREDERIC STANLEY KIPPING was born on August 16, 1863, at Higher Broughton in Manchester. He was the eldest son of James Stanley and Julia Kipping and had two brothers and four sisters. His father held a post in the Manchester branch of the Bank of England of which his paternal grandfather was head. His grandfather on his mother's side was C. A. Duval, a Manchester artist of considerable reputation. James Stanley Kipping played chess against many of the champions of his time, including Paul Murphy, whom he defeated on one occasion when this world champion was playing a number of opponents simultaneously. F. S. Kipping regarded himself as only a moderate player, but his eldest son, C. S. Kipping, headmaster of Wednesbury High School, inherited his grandfather's skill and is a composer of chess problems of worldwide repute and has edited various chess journals.

Kipping early acquired that interest in open-air life which was never to leave him. His father owned a small farm near Higher Broughton, which was at that time practically in the open country. Here he made himself generally useful and gained a fair knowledge of animals and practical agriculture. In the early days the Kipping children had a governess, but at the age of eleven Frederic Stanley entered Manchester Grammar School on the same day as Herbert Brereton Baker. (It is remarkable that both these boys became Longstaff Medallists of the Chemical Society.) He had already become interested in chemistry through his father's friend and neighbor, J. Carter Bell, the public analyst for Cheshire, who showed him various simple precipitation reactions in inorganic chemistry, and advised his father to make him an analytical chemist. No doubt at this time that honorable profession was still generally regarded from the Dickensian point of view, so clearly indicated in "Our mutual friend."

These early influences were strengthened by the teaching of Francis Jones, of whom H. Brereton Baker (*Trans. Chem. Soc.* 1926, p. 1021) wrote: "Besides Jones's personality, what affected

us boys most was seeing him always at work on research. Many of those who have since given their lives to original investigation owe most of the impetus which has driven them on, to the work on boron hydride which they watched in progress. No school-master had an influence like his on the making of a chemist." Kipping remarks that the practical chemistry at Manchester Grammar School consisted almost entirely of qualitative analysis but unaccompanied by any clear explanation of its principles. During the holidays he assisted Carter Bell with the ordinary routine analysis of water, milk, and other foodstuffs. He also spent a year at the Lycée de Caen where food and sanitary arrangements were poor but the teaching of Latin was especially good. Kipping matriculated at the University of London in 1879 in the first division and thereupon entered Owens College, Manchester, his family having meanwhile removed to Platt Abbey, a house familiar to this day to all those who travel on a 42 'bus along the Palatine Road to the Burlington Street laboratories. After three years, in which he studied mathematics, physics, botany, chemistry, and zoology, he graduated B.Sc. (London) with second-class honors in zoology. He found Miles Marshall, the professor of zoology, an excellent and inspiring teacher, and Roscoe extremely kind and interested in his students. Schorlemmer, who was the first professor of organic chemistry in this country, did not attract him, however—his lectures were read without emphasis or pause from notes held close to the nose. After a short experience of this mode of presentation of organic chemistry, Kipping devoted Schorlemmer's lecture hours to the practice of billiards in an adjacent hotel, thus acquiring a facility which he never lost. On the whole, with the exception of zoology, he found college work dull and unsatisfactory, but he used the five courts a good deal and played cricket and lacrosse.

After graduation as an external student of the University of London in 1882, he obtained a post as chemist to the Manchester Gas Department in Rochdale Road and later at Gaythorne Street. The duties of the post, except for occasional work throughout the night, were not heavy but afforded him very useful and varied analytical experience which, at the age of nineteen, may have laid the foundation of the scrupulous care and accuracy of his re-

search work. He had plenty of time for reading and was frequently able to leave the laboratory at 4:30 to 5:00 p.m. to catch a train on the former M.S.J. and A. Railway to Old Trafford in order to play tennis at the Northern Lawn Tennis Club. Here, and on many other grounds, he played in matches against the leading clubs of Lancashire and adjoining counties. He remained in the service of the corporation for about three years, to the age of twenty-three. Until then he seems to have shown no particular signs of devotion to chemistry although he was doubtless maturing. About this time, however, a friend of his family, Dr. Adolf Lieberman, a chemist at Levinstein's, strongly advised a period of study in Germany and pointed out the lack of opportunity for advancement in Kipping's post at the gasworks.

Following this advice he entered the University of Munich in the spring of 1886 and was there given a working bench in one of the organic laboratories which was supervised by W. H. Perkin, Jr., who had entered von Baeyer's institute in 1882. There he carried out various organic preparations, and after some months commenced research under Perkin's guidance on the synthesis of closed carbon chains. Thus began a scientific association which was to last until the death of Perkin in 1926 and was destined to influence the lives of both men, not only on the scientific but also on the personal side. Late in 1886 Perkin returned to England and thenceforward Kipping continued his research unaided except for the written advice which Perkin sent him from time to time. At that time Claisen, Bamberger, and von Pechmann were *Privat-docenten* and Nef was a student. Work in the laboratory began at eight and continued till six or after, with a rather long interval for *Mittagessen*—and chess. There was much skating in the winter. Kipping saw very little of von Baeyer. He refers to one occasion, however, on which he showed him with some pride a product he had isolated. The *Geheimrat* looked at it under a lens, snapped out "Ach, Harz" and stalked away. This may have been the origin of Kipping's critical, and, to say the least, realistic attitude to his students' laboratory efforts. However, he took his Ph.D. degree *summa cum laude*, after which he returned to England, and for a short time assisted his father, who had turned his attention to chemical manufacturing on the small scale. The preparation of

sulfur chloride and of carbolic disinfecting powder in the stables of Platt Abbey were not very congenial or successful ventures and did not last very long.

In the autumn of 1887, T. E. Thorpe and Emerson Reynolds, as examiners for the University of London, awarded Kipping the degree of D.Sc. He was the first candidate on whom this degree was conferred on the grounds of research. It would appear, however, that his Munich work sufficed for both his doctorates, a happy state of affairs which would not now commend itself to faculties of science. Immediately afterwards he was offered the post of demonstrator under W. H. Perkin, Jr., who had by now been appointed professor of chemistry at the Heriot-Watt College in Edinburgh. The remuneration was £20 a year "with prospects". Most of the teaching was done in the evening, but Kipping was usually on duty for most of the day, spending much time in research, again under Perkin's direction. In March, 1888, he married his cousin, Lily Holland, the daughter of W. T. Holland, J.P., of Bridgwater, and granddaughter of C. A. Duval. During their engagement Perkin met his future wife, Miss Holland's elder sister, at the house of Kipping's parents.

During the Edinburgh period the writing of the famous "Organic Chemistry" (Perkin and Kipping) was begun. This work was one of the earliest textbooks on the subject, and was first published in 1894. It has enjoyed an enormous reputation and has passed through many editions, the latest of which (1949) presents an excellent picture of the present-day position of the science. After about a year at the Edinburgh College, Kipping was made assistant professor of chemistry and lecturer in agricultural chemistry at a total remuneration of £150 a year.

In late 1890 an event occurred which greatly influenced his future work and afforded him many stimulating contacts and the opportunity of directing the research of beginners. H. E. Armstrong, to Kipping's "astonishment and satisfaction," offered him the post of chief demonstrator in the chemistry department at the Central Technical College of the City and Guilds of London Institute at £240 a year. (The college is now incorporated in the Imperial College of Science and Technology and the chemistry department closed. Many will remember the heated discussion

which took place about 1910 regarding the wisdom of this step, Armstrong having built up a most flourishing school of research.) Kipping accepted this offer "with alacrity" and he and his wife removed from Graham Street, Edinburgh, to a small house at 7 Milborne Grove, South Kensington, Kipping then worked with Armstrong for a time, first on certain problems connected with colour and constitution and then on the products of the action of sulfuric acid on camphor, one of which was shown to be 3:4-dimethylactetophenone (*p*-acetyl-*o*-xylene). This led to a study of a crude sulfonation product of bromocamphor prepared by W. J. Pope, who was at that time lecture assistant to Armstrong. Thus began the fruitful association of Kipping and Pope which lasted for six years, during which many joint papers were published.

Shortly afterward (1893) Arthur Lapworth arrived in Pope's laboratory from Birmingham, where his father was the distinguished professor of geology, and was placed under Kipping's supervision. Here again a very successful collaboration resulted, the work being mainly on derivatives of camphor. Kipping contributed, many years later, a warm tribute to Lapworth which was quoted by Sir R. Robinson in his obituary notice. "Although he was considerably my junior in age, we soon became fast friends; perhaps it would be truer to say that our relationship, even in those early days, was rather that of congenial brothers. He became a frequent visitor at our house in South Kensington where he often met Pope, Forster and other workers in Armstrong's laboratories. During one vacation when he had made no holiday plans, we asked him to stay with us at Bridgwater: here it was that he met his future wife, Kathleen Holland."

The work of Perkin, Kipping, and Lapworth has left a lasting impression on experimental and theoretical organic chemistry which may perhaps best be realized if we attempt for a moment to consider what the record of the years 1895–1930 would be if the work of these three men were left out of consideration. That they married three sisters is surely not unworthy of being placed on record.

Kipping has referred to his constant attendance at the meetings of the Chemical Society and to the considerable amount of work which he performed for the Society's *Abstracts*. He mentions that the leading figures at the meetings after Armstrong (Secretary

"and chief manager even when not himself the President") were Dewar, Ramsay, Dunstan, M. Lamb, Groves (Editor), Greenaway (Sub-Editor), Sir William Crookes ("who was very kind to young chemists"), Perkin, Sr., R. Messel, Pickering, J. M. Thompson, Gladstone, Collie, Sir Frederick Abel, Chattaway, Pope, Lapworth, and Forster.

He found little time for recreation but whenever possible he and his wife went for long rowing excursions on the Thames, returning only when the light faded. During six years they heard, from the gallery of Covent Garden Opera House, nearly all the great operas and most of the famous singers of the day.

In 1897 Kipping was elected to the Royal Society at the age of thirty-four, and soon afterwards was appointed to the chair of chemistry at University College, Nottingham, in succession to Professor Frank Clowes. He found the laboratories and classrooms in Shakespeare Street compact and well-arranged, but there were only four full-time students who were working for the Associateship of the Institute of Chemistry, the remainder consisted of a few ill-prepared part-time students of engineering. Most of the evening students were working for the qualifying examination of the Pharmaceutical Society. He refers to certain short courses given in those early days to students of mining, dyeing, plumbing, and brewing, and adds: "I came to the conclusion that such so-called technical education was valueless . . . the more intelligent students of these subjects were encouraged to attend the evening classes in pure chemistry during two or three years, and their practical work was so arranged that it had a direct bearing on their daily occupations." The number of students of chemistry steadily increased, and Kipping, first unaided, and then in collaboration with members of his staff, initiated various lines of research which will be considered later. He also acted as external examiner to the federal Victoria University and to the Royal University of Ireland, and much appreciated the kindness and hospitality of Professor Dixon of Cork and Professor Senier of Galway, but greatly regretted the necessity of failing so large a proportion of the Irish candidates. Both before and after the First World War he was external examiner to the University of Birmingham and wrote in 1942: "There the standard was high, and the unfailing kindness of

Professor and Mrs. Frankland with whom I stayed remains a most pleasant memory even now."

During the First World War, Kipping and his staff collaborated in the scheme for the preparation of synthetic drugs which were at that time unobtainable in Britain; he also lectured on musketry and map-reading to the Officers' Training Corps and superintended practice on a miniature rifle range in an old clay pit.

Like all other chemistry departments of university rank, Kipping's laboratories were crowded after the armistice of 1918, and it became necessary to find immediate temporary accommodation for the forty or fifty full-time students who wished to work for the Pass and Honours degrees of the University of London. The Shakespeare Street buildings of the College were situated between the City Library on the one side and the City Museum on the other, forming one large block which was and is a familiar—and I think pleasing—aspect of Nottingham. To meet the demand, one of the large rooms of the museum was cleared of its stuffed animals and converted to a laboratory, capable of providing about seventy working benches for the more elementary and part-time students. This met the immediate needs, but after 1922 it became obvious that the student population of the College as a whole would remain permanently at a much higher figure than that obtaining before the war.

The College Council thereupon decided to build a new University College. Fortunately this was made possible through the great generosity of Sir Jesse Boot, later Baron Trent, who not only purchased the splendid site now known as University Park, but also defrayed the cost of the building and equipment and endowed the chair of chemistry, Kipping thus becoming the first Sir Jesse Boot Professor of Chemistry. The college was opened by H. M. King George V in 1928.

In 1936, after the College Council had, on several occasions, refused to accept his offers to resign, he retired from the chair and was appointed emeritus professor of chemistry. The Council made arrangements for him to work in his old laboratory at Shakespeare Street, and there he continued research on silicon compounds till the outbreak of war in 1939 when he and Mrs. and Miss Kipping removed to Criccieth. Shortly after his retirement the University of

Leeds conferred upon him the degree of D.Sc. *honoris causa*, in recognition of his long services to university teaching and research.

In the same year, soon after Kipping published Part L of *Organic derivatives of silicon*, his staff and former students entertained him to dinner. Robison, the discoverer of the mechanism of the calcification of cartilage, was in the chair, and over seventy were present. It was a most happy and inspiring occasion; the respect and affection in which Kipping was held were manifest in every word which was spoken. The dry, humorous remarks, the caustic comments, the rather gruff encouragements stored for many years in the memories of his pupils were then released in the speeches. Happy is the man who can inspire such regard.

For a year or two after his retirement he continued to supervise the work of a few research students and published one more paper, Part LI, which was unique in one respect. At the end it contained these words. "*Envoi*. As this is my last paper may I express here my sincere thanks to the Chemical Society for having published so much of my work over so long a period—F. S. K." I do not recall a similar acknowledgment by any other Fellow of the Society.

On the outbreak of war in 1939 Kipping, with his wife and younger daughter, took a house on the sea front at Criccieth and there it was my privilege to see him in 1946 and 1947. He was surrounded by the proofs of the revised, almost rewritten, edition of "Perkin and Kipping," in the production of which he had been joined by his younger son, Frederic Barry, university lecturer in chemistry in the University of Cambridge. He was, it need hardly be mentioned, as interested as ever in the progress of chemical research and in the forthcoming promotion to university status of the old college at Nottingham. It must have been a source of considerable satisfaction to Kipping that his son not only entered academic life, but, like his father, collaborated with Pope on various stereochemical themes. F. B. Kipping has also published much independent work in general organic chemistry and in stereochemistry.

In the spring of 1949 the health of Mrs. Kipping caused him much anxiety, and after only a week's illness he died on May 1 in his eighty-sixth year.

Kipping's interest in derivatives of camphor was due to his

association with Armstrong at the Central Technical College. Kipping states: "Armstrong then asked me to examine a crude sulphonation product of bromochamphor prepared by W. J. Pope; thus began the joint research work which extended over six years during which period many joint papers were published."

The first paper described the sulfonation of camphor and bromocamphor with anhydrosulfuric acid or chlorosulfonic acid. "The camphor-sulphonic chloride prepared from the acid obtained by either of these methods is a mixture of optical isomerides, but as the dextro-rotatory modification is present in rather the larger proportion we have been able to isolate and examine it. The optically inactive, or feebly active, mixture of sulphonic chlorides shows a very remarkable behaviour; it is deposited from solution in well-defined crystals which, although apparently homogeneous, are simply mixtures of the two active compounds in variable proportions and are partially resolved into enantiomorphous forms on recrystallization.

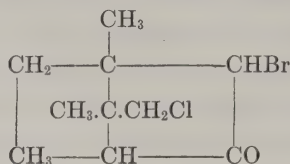
"The sulphonic derivatives of bromo- and chlorocamphor are optically active and remarkable for the extraordinary facility with which they crystallize; the sulphonic chlorides, the amides, the acids and a number of salts are described, the optical and crystallographical characters of many of the compounds being given." Such details appeared in many subsequent papers published by Kipping throughout his life, both in collaboration with Pope and with other workers. The importance attached to crystallography by other pupils of Armstrong, e.g., Lowry, is well known.

The authors add: "Speaking generally the sulphonic derivatives of camphor are compounds of exceptional beauty [here, surely, we detect the Perkin touch] and judging from the results thus far obtained will probably lead to conclusions of considerable importance." When we consider the part played by bromocamphorsulfonic acid in almost every study of optically active bases during the last fifty years, this prophecy may be regarded as entirely justified.

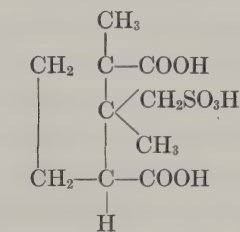
In two further communications Kipping and Pope extended their detailed study of camphorsulfonic acids and their derivatives, and showed that the preliminary effervescence observed during the combustion of sulfonic halides of camphor and its halogen derivatives is due to the evolution of sulfur dioxide and formation of the

so-called π -halogen derivatives (so named owing to their pyrogenic formation), in which the atom so introduced replaces the $-\text{SO}_2\text{Hal}$

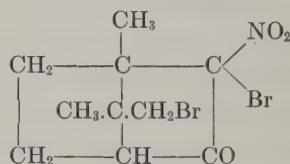
group in the $\text{CH}_3-\overset{\textstyle |}{\text{C}}-\text{CH}_2\text{SO}_2\text{Hal}$ residue of camphor. Thus
 $\text{bromocamphorsulfonic chloride}$ yields α -bromo- π -chlorocamphor



Many derivatives of this type were obtained, and in several papers published in collaboration with Lapworth (whose first research at the Central Technical College was carried out under Kipping's supervision) their properties and those of other derivatives of camphor, especially nitrocamphor and camphoric acid, were carefully examined. The titles listed in the bibliography indicate the scope of this work. Lowry's work on bromocamphor, mutarotation, and similar themes was also an outcome of the assiduous cultivation of the camphor field in South Kensington at the turn of the century. Two of the compounds investigated by Kipping alone or in collaboration with Lapworth may be mentioned in passing:



Sulfocamphoric acid

 α - π -Dibromo- α -nitrocamphor

Reference may here be made to two stereochemical investigations in one of which Kipping and Salway approached the vexed question of the "Arrangement in space of the groups combined with the tervalent nitrogen atom" and the other, where, with his student, Peters, he investigated "Iodonium compounds of the type $\text{IR}'\text{R}''\text{R}'''$ " and the configuration of the iodine atom" (*T.* 1902, **81**, 1350).

The work of Kipping and Peters on iodonium compounds consisted in the fractional crystallization of phenyl-*p*-tolyl-iodonium *d*-bromocamphorsulfonate. Not the slightest evidence of resolution could be obtained.

Between 1900 and 1905 Kipping published a series of eleven papers entitled "Isomeric partially racemic salts containing quinquivalent nitrogen." All of these except the last were published under his name only. The work arose out of experiments on the resolution of *dl*-hydrindamine which were later extended to *dl*-methylhydrindamine and *dl*-benzylhydrindamine. The resolution of the first two bases was successfully achieved and the active components proved of the greatest service in later work; the *d*- and *l*-methylhydrindamines were, in fact, essential to Kipping's most outstanding success. Before the *d*- and *l*-bases could be separated, however, much exploratory work had to be carried out, and many of the observations which were made during the course of the almost endless fractional crystallizations were most unexpected and confusing. The research, in fact, offered numerous opportunities for the exercise of the skill, care, and patience which characterized all Kipping's work. The somewhat tentative explanation which he put forward to account for the unexpected results was, at the end of five years, replaced by the correct one, and he was able to say, "Nevertheless all the old facts remain as recorded, and as regards the experimental part of the work there is, as far as the author knows, nothing to correct and nothing to withdraw." (*T.* 1905, **87**, 636.)

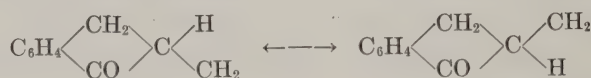
The main results of this work will now be described as briefly as possible. (*T.* 1900, **77**, 861.)

"When *dl*-hydrindamine is combined with various optically active acids it shows an altogether unusual behaviour, giving in some cases what appears to be a homogeneous partially racemic salt, in others a mixture of unequal quantities of two isomeric salts; the latter are not the ordinary isomerides which are obtained from most externally compensated bases under such conditions. They do not represent salts of the separate enantiomorphously related components of the base, but are both comparable to partially racemic substances."

dl-Hydrindamine and α -bromocamphorsulfonic acid unite to form

unequal quantities of two salts containing different quantities of water of crystallization . . . absolutely different in appearance and with different specific rotations. Hydrindamine and chlorocamphorsulfonic acid give unequal quantities of two isomeric salts which are respectively analogous to those of the bromo-acid. These two series of salts were designated α - and β - by Kipping. The conversion of either of these α -salts (bromo- or chloro-) into the corresponding β -salt or vice versa by crystallization only, has never been observed.

Kipping came to the tentative conclusion that the isomerism was due to stereoisomerism among the groups attached to the quinquevalent nitrogen atom but the arguments do not lend themselves to summarization, especially after the lapse of fifty years. Five years later, however, the conditions under which the β -salt could be converted to the α -modification were accidentally established during an attempt to convert β -*l*-hydrindamine bromocamphorsulfonate into the β -*l*-chlorocamphorsulfonate. He finally showed that the production of the so-called α - and β -salts was due to the existence of *cis* and *trans* forms of the bromo- and chlorocamphorsulfonic acids which are convertible through the unstable enolic form. In support of this stereochemical explanation, Kipping quotes the rapid racemization of *d*-methylhydrindone in presence of alcoholic sodium ethoxide



doubtless by passage through the unstable enolic form.

Kipping's work on organic derivatives of silicon was commenced with the object of obtaining compounds of which the optical activity was due to the presence of an asymmetric silicon atom, and clearly arose out of his work on the stereochemistry of nitrogen. This, in its turn, was probably a consequence of his still earlier interest in camphor. It might be imagined that the discovery of the Grignard reagent was a determining factor in Kipping's choice of this field of research; but although the progress of his work was greatly eased by the use of these reagents, the research was commenced one or two years before 1900 (the year in which Grignard

made his initial observation), and in Part I Kipping and Lloyd make no reference to the French chemist's discovery.

Kipping's work in this field, which extended over a period of nearly forty years, may be regarded under three main headings: (1) experiments connected with the preparation and resolution of asymmetric compounds of silicon, (2) work on the structure of the simpler condensation products derived from compounds of the type $R_2Si(OH)_2$ and $RSi(OH)_3$, and (3) the study of the products obtained from arylchlorosilanes R_2SiCl_2 or $RSiCl$ and sodium. Of these three main lines, the first attracted great attention at the time, the other two were disregarded.

Since 1940 the extension of the second line of work under the auspices of the Dow Corning Corporation has brought his name to the notice of hundreds who had never heard of him previously. Kipping certainly spoke truly when, in 1912, he remarked to a student who had used the term "polymerization" loosely and rather carelessly: "Polymerization, that's a blessed word, it's like Mesopotamia." The personal application of this comment was not apparent for nearly thirty years. His former students and colleagues welcome the utilization of his silicols and silicones, but deny with much warmth that this publicity adds anything to his scientific reputation, which was firmly established many years before the plastic age commenced. Their "welcome" is accorded rather to the demonstration, so frequently made but so readily forgotten, that no limit can be placed to the results which may spring from careful scientific investigation carried out for its own sake and for no other reason.

The reactions employed by Kipping for the synthesis and, in three cases, resolution of his asymmetric compounds were simple in the extreme, but the experimental difficulties were considerable.

In Part I, three chlorine atoms of silicon tetrachloride were successively replaced by the phenoxy, methoxy and ethoxy groups, but attempts at resolution, by replacing the fourth chlorine atom by the methoxy group or by the anion of an optically active acid, were unsuccessful.

Five other asymmetric compounds of silicon were prepared between 1905 and 1910 by the successive replacement of the chlorine

atoms with alkyl and aryl radicals by means of the Grignard reagent. The sulfonic acids of *dl*-benzylmethylethylpropylsilicane and *dl*-benzylmethylpropylisobutylsilicane resisted all attempts at their resolution, although numerous optically active bases including cinchonidine, cinchonine, *l*-menthylamine, strychnine, brucine, and quinine were employed.

His first success was obtained by the sulfonation of *dl*-phenylbenzylethylpropylsilicane. When using sulfuric acid at ordinary temperatures or below 70° C. benzene is eliminated (but not toluene), probably with formation of $\text{Si.Et.Pr.CH}_2\text{Ph.OH}$ which then yields the disulfonic acid of the oxide $(\text{Pr.Et.CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H.Si})_2\text{O}$. This elimination of benzene appears to be characteristic of the Ph-Si link under such conditions. Later on he used chlorosulfonic acid instead of sulfuric acid, obtaining the same sulfonic acid.

Kipping finally isolated a crystalline, deliquescent di-ammonium salt of this acid, of which he remarks in a footnote, "This was the first crystalline silicon compound obtained during at least six months' work, so the author has been careful not to over-rate its beauty."

This acid was also obtained by the sulfonation of benzylethylpropylsilicol, obtained by the action of water on the corresponding chloride (Part II), and also (Part IV) by sulfonation of benzylethylpropylsilicyl oxide $(\text{R}_1.\text{R}_2.\text{R}_3.\text{Si})_2\text{O}$. Kipping then conclusively showed by numerous analyses of the *l*-methylamine salt, that the sulfonic acid was a derivative of the oxide and not of the silicol. Attempts to resolve this acid by fractional crystallization of the *l*-menthylamine, *d*-bornylamine, cinchonidine, cinchonidine hydrogen, and strychnine salts were unsuccessful, but with *d*-methylhydrindamine resolution was accomplished, although much care was needed in interpreting the results owing to the low specific rotation of the *d*- and *l*-sulfonic acids. Thus on crystallizing the *l*-methylhydrindamine salt of the *dl* acid sparingly and readily soluble fractions, differing widely in m.p. but not in specific rotation, were obtained (Part II). Expulsion of the volatile base and conversion to the *l*-menthylamine salts gave products which did not differ appreciably in either m.p. or specific rotation. By suitable

alternate use of the volatile *l*- and *d*-methylhydrindamines by methods which are obvious and need not be described in detail, it was conclusively proved that resolution had occurred, the *dAdB*, *lAlB*, *dAlB*, and *lAdB* (where A and B represent acid and base), salts being very carefully compared. Finally, by removal of the volatile bases two sodium salts of specific rotation $+5.8^\circ$ and -5.9° were obtained (Part VI).

It is interesting to speculate as to whether, had it not been for the unexpected elimination of the phenyl group during the sulfonation of phenylbenzylethylpropylsilicane, Kipping would ever have studied the sulfonation of an asymmetric silicol or oxide. Had he not done so the negative results obtained with two sulfonated silicanes suggest that success might never have been achieved. Still more remarkable is the coincidence that the only bases which were found capable of resolving the sulfonated silicyl oxides were the *d*- and *l*-methylhydrindamines which he had himself prepared for the first time in the course of earlier work and submitted to a most exhaustive examination.

A year or two later, in collaboration with B. D. W. Luff, he carried out a successful resolution of the disulfonic acid of *dl*-benzylethylisobutylsilicyloxiide, also by the aid of the *d*- and *l*-methylhydrindamines, thus amplifying and confirming his earlier results. In this case the specific rotations of the sodium salts were larger, $+10.4^\circ$ and -10.5° .

Several years later Kipping prepared *dl*-dibenzyl-diethyldipropyl-silicoethane and obtained brucine and *l*-menthylamine salts of the disulfonic acid. Separation of the racemic and meso forms of the acid or the resolution of the first-named was not effected, owing to lack of material (Part XXIV). With reference to this hydrocarbon and the corresponding diphenyl compound, Kipping writes: "Although their molecules contain linked silicon atoms both silico-hydrocarbons are attacked only very slowly if at all by boiling aqueous alkalis, and even when they are warmed with sodium methoxide in methyl alcohol or acetone no rapid evolution of hydrogen is observed. The grouping $\rightarrow\text{Si-Si}\leftarrow$ is not necessarily unstable to alkalis, and whether the silicon atoms become separated or not is determined by the nature of the atoms or groups with

which they are combined." The behavior of the $\rightarrow\text{Si-Si}\leftarrow$ link to alkali is also mentioned.

During the purification of benzylethylsilicon dichloride which was so important an intermediate compound in much of his work, Kipping isolated dibenzylethylsiliclylchloride $(\text{PhCH}_2)_2\text{SiEt.Cl}$. This was converted to dibenzylethylpropylsilicane and sulfonated, using chlorosulfonic acid in chloroform (Part XII). After separation of the mono- and disulfonic acids by means of their strychnine or *l*-menthylamine salts, the monosulfonic acid was successfully resolved by brucine but by no other base although several were employed.

Shortly afterwards Kipping and T. A. Smith prepared the tin analog of the silicane, dibenzylethylpropylstannane $(\text{PhCH}_2)_2\text{-Sn.Et.Pr}$, but the sulfonation of this and of dibenzyl-diethylstannane was impossible owing to the elimination of both the benzyl groups by the acid.

About this time Kipping returned to the study of a similar problem on which Caven (*T.* 1902, **81**, 1362) had already carried out experiments in his laboratories—the stereochemistry of asymmetrical derivatives of phosphoric acid. Caven had been unable to

resolve compounds of the type $\text{O}=\text{P}\begin{matrix} \text{NHR} \\ \text{NHR}' \\ \text{OH} \end{matrix}$. Kipping and Luff

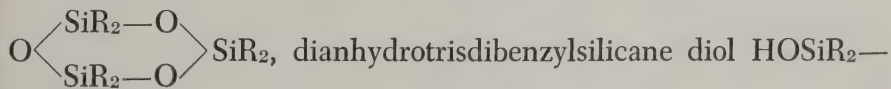
prepared phenyl *p*-tolyl hydrogen phosphate $\text{OP}(\text{OPh})(\text{OC}_7\text{H}_7)\text{-OH}$ and crystallized its salts with eight optically active bases without effecting resolution. Evidence that the acid was, in fact, a *dl*-compound was obtained by the separation of the *dl*-hydrindamide into two inactive compounds, the *dAdB*, *lAlB* and the *dAlB*, *lAdB* isomers. By crystallization of the *d*-hydrindamide and *l*-menthylamide two fractions differing in m.p. and specific rotation were obtained in each case, indicating a resolution of the *dl*-acid. Similar results were obtained by Kipping and Challenger with the *l*-menthylamide of phenyl- β -naphthyl hydrogen phosphate. In none of the cases was it possible to remove the optically active -NHR group by hydrolysis so as to obtain the corresponding acids. This stability appears to be characteristic of amides and substituted amides of this type.

Over thirty years later Davies and Mann (*J. Chem. Soc.* 1944, p. 276) pointed out that these and similar experiments aiming at the isolation of the optically active acids were foredoomed to failure owing to resonance.

When Meisenheimer and Lichtenstadt (*Ber. deutsch. Chem. Ges.* 1911, **44**, 356) announced the resolution of methylethylphenylphosphine oxide Kipping published a second and final paper on this subject.

Some consideration must now be given to the work on the condensation and dehydration products of the dibenzyl- and diphenylsilicanediols $R_2Si(OH)_2$. Much of this was carried out with Robison, who was first a student and later a junior colleague of Kipping.

These investigations do not lend themselves to detailed summary as they were mostly concerned with the careful examination and final separation of mixtures of condensation products, a study of their reactions, in some cases their interconversion and the determination of their molecular weight. The work was laborious and involved much detailed study of closely related substances and the manipulation of intractable oils, many of which were finally induced to crystallize. Kipping realized from the beginning (see Part X) that the various so-called silicones, e.g., Et_2SiO , Ph_2SiO and $Ph.Et.SiO$, were associated and not simple molecules; this was in fact stated by Dilthey in the case of the diphenyl derivative in 1905. In his first paper with Robison (Part V) Kipping studied the loss of water from dibenzylsilicanediol $(PhCH_2)_2Si(OH)_2$, and in Parts XVIII and XX established that under various conditions the diol yield trianhydrotris(dibenzylsilicane) diol



$O-SiR_2-O-SiR_2.OH$ and anhydrobis(dibenzylsilicane) diol $HOSiR_2-O-SiR_2.OH$ where $R=CH_2C_6H_5$. Heat or alcoholic hydrogen chloride, acetyl chloride or alkali were employed as condensing agents.

During this period a similar and even more extensive study of the condensation products of diphenylsilicanediol was carried out,

and in three papers, Parts XVI, XVII, and XXI, the existence of five crystalline condensation products was established, namely, $\text{HO.SiPh}_2\text{—O—SiPh}_2\text{.OH}$, $\text{HO.SiPh}_2\text{—O—SiPh}_2\text{—O—SiPh}_2\text{—OH}$, $\text{HO.SiPh}_2\text{—O—SiPh}_2\text{—O—SiPh}_2\text{—O—SiPh}_2\text{.OH}$



In the case of four of these products crystallographic measurements were carried out.

When dichlorosilanes of the type RR'SiCl_2 are decomposed with cold aqueous ammonia the corresponding diols, e.g., benzylethylsilicanediol and phenylethylsilicanediol RR'Si(OH)_2 , are obtained (Part XIX), and from the second of these the crystalline condensation product $\text{HO.SiPhEt.O.SiPhEt.OH}$ can be isolated. Kipping refers to the ease with which these two diols yield oily condensation products, probably of the types already established in the case of diphenylsilicanediol, and adds "as the components of these mixtures have doubtless much lower melting-points than the corresponding derivatives of diphenylsilicanediol they cannot be isolated by the methods which were found to be of service in the case of the latter compounds." These substances containing alkyl groups foreshadowed the numerous polymers derived from $\text{Alkyl}_2\text{Si(OH)}_2$ which have since found such important technical applications. So far as can be seen from Kipping's papers he found no evidence for the existence of the simple silicones R_2SiO .

Only by a careful study of the original papers is it possible to realize the complicated relations existing between these various condensation products and the experimental skill and patience required for their separation from still more complex substances.

With his student Meads he also examined the condensation products obtained by the hydrolysis of phenyltrichlorosilanes which are derived from four, five, six, or more molecules of PhSi(OH)_3 . Here, and in many of his papers, he drew attention to the possible analogy between the structure of these compounds and that of the silicates, and between $\text{HO.Sn(C}_7\text{H}_7)_2\text{.O.Sn(C}_7\text{H}_7)_2\text{—O—Sn(C}_7\text{H}_7)_2\text{—OH}$ and the polymeric stannic acids. He also found that $(\text{C}_7\text{H}_7)_3\text{SnOH}$ is strongly associated in benzene solution (*J. Chem. Soc.* 1913, p. 2034).

It is a pleasure to recall that the Dow Corning Corporation presented him in 1945 with a complete set of his fifty papers on "Organic derivatives of silicon" very clearly typed on strong paper and bound in boards made from a "silicone" polymer. These three volumes he presented to the Royal Society and they have been of great help to the writer in preparing this memoir.

No one who worked in the Nottingham laboratories between 1907 and 1910 will have forgotten the riddle of the constitution of the yellowish-white, amorphous, insoluble organic substances which are produced as by-products when any Grignard compound reacts with silicon tetrachloride. When all organosilicon halides are removed from the mass of magnesium salts with ether and these salts are dissolved in water, these compounds remain. Their most striking property is the rapid effervescence of hydrogen which takes place on addition of potassium hydroxide. Kipping never published a full account of these substances although he worked on them from time to time. It soon became clear that these compounds contained $\rightarrow\text{Si-Si}\leftarrow$ links. The evolution of hydrogen would seem to be analogous to that observed when silicoethane Si_2H_6 , silico-oxalic acid $\text{H}_2\text{Si}_2\text{O}_4$, silicomexoxalic acid and similar compounds are treated with alkali. In the case of the ethyl compound, Martin and Kipping suggested the possible structure $\text{C}_2\text{H}_5\text{Si}(\text{OH})_2\cdot\text{SiO}_2\text{H}$. The formation of such compounds was particularly marked in the case of the cyclohexyl derivatives, volatile chlorides containing $\rightarrow\text{Si-Si}\leftarrow$ links being detected (Part XLII) and light thrown on their method of formation.

Several years later it was found that wet piperidine was a more satisfactory reagent for the fission of the $\rightarrow\text{Si-Si}\leftarrow$ link, and the hydrogen evolved—the "hydrogen number"—was frequently employed as evidence of structure although the reaction was not of universal application, a few compounds such as $\text{Si}_2(\text{C}_6\text{H}_5)_2$ and $\text{Si}_2(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)_2(\text{C}_3\text{H}_7)_2$ being found to resist fission.

On the conclusion of his work on optically active silicon compounds and the condensation products of the diphenyl- and dibenzylsilicanediols, Kipping gave much attention to the reaction between sodium and organosilicon halides of the type R_2SiCl_2 and R_3SiCl . The original object was to obtain a simple unsaturated compound $\text{R}_2\text{Si} = \text{SiR}_2$, but this was never achieved. Diphenylsili-

con dichloride, e.g., gave two crystalline compounds of the formula Si_4Ph_8 , one of which in later work was shown to be octaphenylcyclotetrasiloxane $\text{Ph}_2\text{Si} \begin{smallmatrix} \text{SiPh}_2 \\ \text{SiPh}_2 \end{smallmatrix} \text{SiPh}_2$ whereas the consti-

tution of the other "is best represented by . . . $\text{SiPh}_2.\text{SiPh}_2.\text{SiPh}_2.\text{SiPh}_2$. . ."

This is much more reactive than the cyclic compound. It slowly changes on exposure to light and air and undergoes atmospheric oxidation in toluene at 100°C ., it combines with iodine at ordinary temperature giving a diiodide and is readily attacked by ethylene dichloride and tetrachloroethane, giving products which after hydrolysis contain oxides, $\text{Ph}_8\text{Si}_4\text{O}$ and $\text{Ph}_8\text{Si}_4\text{O}_2$, one of which is

$\text{Ph}_2\text{Si}-\text{SiPh}_2 \begin{smallmatrix} | \\ \text{Ph}_2\text{Si}-\text{SiPh}_2 \end{smallmatrix} \text{O}$. The structure of the dioxide and an isomeric dioxide are discussed in Parts XXV and XXVI.

In 1932 Kipping and Blackburn (Part XLVI) showed that nitration of tetraphenylsilicane yielded a small amount of a pure nitro compound which, on decomposition with bromine, gave *m*-bromonitrobenzene. The main product of nitration, however, was extremely ill-defined and with bromine yielded a mixture of *m*- and *p*-bromonitrobenzene approximately in the proportion of 2:1. The occurrence of *o*-nitration was not established. The pure tetranitro compound was reduced to the corresponding amine, which was thoroughly examined.

Part L of "Organic derivatives of silicon" is noteworthy as marking the author's Jubilee and also because it emphasized his definite, although late, entry into the field of aromatic substitution. Had he undertaken work of this kind earlier most interesting results would no doubt have been forthcoming. The paper describes the nitration of phenyltriethyl-, diphenyldiethyl-, and triphenylethylsilicanes PhSiEt_3 , Ph_2SiEt_2 and Ph_3SiEt . A comparison of the bromonitrobenzenes obtained from the resulting crude products of nitration with those obtained from crude nitrated tetraphenylsilicane showed that *m*-nitration diminishes and *p*-nitration increases as the phenyl groups are replaced by ethyl groups. " $-\text{SiPh}_3$,

FREDERIC STANLEY KIPPING

in fact, is more strongly *m*-orientating than -CCl_3 , although rather less so than NO_2 ."

When more than two phenyl groups were present in the silicanes the nitration product was found to be mainly of a very ill-defined nature. Kipping thought it probable that *m*- and *p*-nitration might occur in the same molecule.

Selections from: *Obituary Notices of Fellows of The Royal Society*,
7, No. 19, 183 (1950).

FREDERICK CHALLENGER

.. 82 ..

Leo Hendrik Baekeland

1863-1944



LEO HENDRIK BAEKELAND lived a life that to chemists must seem nearly ideal—it was filled with accomplishments and satisfactions, a busy life that earned him much wealth and many honors. He was most happily married and his friends were an international legion.

Baekeland was, as his close associate L. V. Redman described him, “truly a great creative chemist.” Yet being Continental-born, he was not driven by that compulsion which kept so many American leaders of his generation on the treadmill of their own ambitions. He took time to enjoy good living, books, music, sports, and hobbies. His life was therefore exceptionally well-rounded.

He was born in Ghent, Belgium, November 14, 1863. His parents, Karel and Rosalia (Merchie) Baekeland, were not prominent or wealthy people. But they were responsible, respected citizens of the ancient Flemish city and they gave their son ideals and principles which were the foundation of his own character.

The boy attended the public schools where from the first grade he was a brilliant pupil. Always at the head of his class, he displayed phenomenal intellectual capacity. While at high school, he took on extra night courses in chemistry, physics, mechanics, and economics, and on graduation day—he was sixteen, the youngest boy in the class—he carried off four medals and a government scholarship at the University of Ghent. In 1884, at twenty-one, he received his doctorate in the natural sciences, *maxima cum laude*.

At the University Baekeland studied chemistry under Edward Swartz, formerly assistant to Kekulé, discoverer of the benzene ring. Professor Swartz, an inspiring teacher, made this precocious student his laboratory assistant, and on the side, Baekeland earned more money by private tutoring. He was, by this time, supporting himself without help from his father. Thus at an early age he exhibited some of his marked characteristics: a thrifty sense of money values, the ability to write and speak effectively, and his independent spirit.

In 1887 he was named by the government professor of chem-

istry and physics at the Higher Normal School at Bruges. The following year he was back in his native city as assistant professor of chemistry at the University. In 1889 he was promoted to associate professor. While at Bruges he won a signal honor. In competition with the graduates of the four Belgian universities, he won the title of Laureate in Chemistry, a gold medal, and a three-year traveling fellowship.

Baekeland had not the least intention of spending three years in the laboratories of great-name chemists at various universities. He knew he was well grounded in chemistry. His ambition was to apply his knowledge practically and profitably. Besides, he was very much in love with Celine Swartz, the pretty daughter of his old professor.

Accordingly he postponed his fellowship until he could use it to finance a prolonged honeymoon trip combined with a chemical scouting expedition. He stayed at Ghent, teaching, and laid siege to the charming young lady. They were married August 8, 1889.

Leo and Celine Baekeland started their honeymoon by visiting French and British universities. We can guess the nature of his inspection of their faculties and laboratory facilities from the point of view he expressed in an address years later:

My real chemical education began only after I left the university and was confronted with the big problems and grave responsibilities of practical life, and this education I received mainly in the United States. I hope to remain, until I die, a post-graduate student in that greater school of practical life which has no fixed curriculum and where no academic degrees are conferred, but where wrong, petty theories are quickly cured by hard knocks.

All this lay in the future. But even at that time his interest was focused on workaday chemical problems. We can imagine his astonished amusement when at Oxford he was told that "no gentleman works with his hands, but we have a fine collection of books on chemistry."

Nowhere did he find what he was seeking. At Edinburgh he was almost persuaded. There he met that amazing teacher, Crum Brown, surrounded by eager students working in fine laboratories.

But there were no facilities for testing the results of applied research, and he learned that such mundane matters were considered quite undignified. Still seeking an academic niche in which to pursue his practical bent, he and his bride sailed for America.

In New York he found in Professor Charles L. Chandler, a chemist who cherished science for its services to mankind. Also at Columbia University there were both encouragement and opportunities for the kind of chemistry he dreamed of practicing. But a youthful hobby unexpectedly reshaped his entire career.

Since boyhood he had been a keen amateur photographer. Naturally he was interested in the chemistry of photography, and back in 1887 had been granted Belgian Patent No. 78,957, his first of many, for the invention of an automatic self-developing dry plate. A successful manufacturer, Dr. Van Monkhaven of Ghent, bought this patent—it did not prove commercially feasible—and he encouraged young Baekeland to continue working in the chemistry of photography. At a New York Camera Club meeting Baekeland met Richard A. Anthony of E. & H. T. Anthony & Co., later Ansco. Anthony promptly offered a job to this young chemist whose photographic background made him about as rare as a Chinese mandarin on Fifth Avenue. The stunning salary offered the prospective chief (and only) chemist of the Anthony firm clinched the matter. Baekeland accepted the first and only job he ever held.

Two years later, in 1891, ambition and independence spurred him to open his own consulting laboratory where he would be free to develop the chemical ideas that teemed in his virile brain. Clients beat a path to his door. As he learned while laid up several months by a serious illness, he was too successful as a consultant. Gravely appraising his situation, he resolved to simplify his consulting activities and concentrate his own researches upon the one most promising project.

The fruits of this resolution were Velox, the photographic paper that could be printed by artificial light, and the Nepera Chemical Company, organized with the financial aid of his friend, Leonard Jacobi of Yonkers, New York, to manufacture and market this revolutionary photographic specialty. Now it was that he felt those "hard knocks" which he was later to praise so warmly as the best teachers in the school of experience. This new venture was

launched in the financial gale of the panic of 1897. He had the usual troubles in manufacturing his new product on an industrial scale. Most difficult were the least expected problems of sales. He first approached commercial photographers, the largest concentrated market, and here he met that stubborn resistance to innovations in established processes inborn in many businessmen. So he turned to the amateurs and found them more venturesome, in fact, quite keen to find a way of indulging their hobby in the evening hours. By 1899, after a hard struggle, Nepera's annual report showed black figures, and the sales of Velox mounted rapidly.

George Eastman's Kodak sales were also zooming, thanks to his introduction of the roll film. Velox fitted perfectly into Eastman's plans to make photography a great popular hobby, and he wrote that he was interested in buying. Baekeland did not reply for three days—it would not do to appear anxious—and then he answered that he might sell—for a price—and that he would be in Rochester a week from the following Tuesday.

But for what price? The question gnawed at his brain day and night. All the way up on the New York Central sleeper he lay awake, wondering what the aggressive and reputedly hard-boiled Eastman would pay. Not till the train reached Rochester did he come to a conclusion. He would ask \$50,000; he would not accept less than \$25,000.

During breakfast at the Hotel Seneca and driving out to the Kodak offices he rehearsed questions and answers for the coming interview. He was shown immediately into George Eastman's office and greeted cordially.

"Dr. Baekeland, I am delighted to meet you. You have a perfectly wonderful thing in that Velox paper of yours—wonderful, full of possibilities. I have the greatest admiration for your accomplishment. Won't you be seated?"

Baekeland sank weakly into a chair. None of his carefully planned speeches fitted this opening.

"Dr. Baekeland, will you take a million dollars for Velox?"

It was fortunate, as Baekeland told it to me, that he was seated, else he would have sunk through the floor.

His partner, Jacobi, went to California to live, and Leo Baekeland also retired, but to a little laboratory he fitted out on the

grounds of his home in Yonkers. Electrochemistry was in the air, a new and industrially enticing field, so at thirty-six Baekeland went back to school, the Technische Hochschule at Charlottenburg, near Berlin.

He stayed there only one winter semester, and apparently he came to see the sights and enjoy the opera and theater of the German capital quite as much as to profit by the professional opportunities. At least, this was the first impression he made upon a hard-working American fellow student. But young Charles Herty soon learned that, for all his casual manner, this big grasshopper in that hill of busy ants had a profound knowledge of chemistry and amazing chemical abilities. Nothing escaped his quick intelligence in the lecture room; in the laboratory he managed, without seeming effort, to do vast amounts of first-class work.

Upon his return Baekeland was called upon by Elon H. Hooker to iron out a difficulty that prevented continuous operation of the Townsend electrolytic cells installed at the new-built plant of the Hooker Electrochemical Company to produce caustic soda and chlorine. The diaphragms, made of asbestos paper, were short-lived. Baekeland corrected this by using asbestos cloth impregnated with a mixture of iron oxide, asbestos fiber, and gummy iron hydroxide. At this time he was also much interested in air conditioning, food preservation, and various electrical control instruments.

Soon, however, he became absorbed in getting a superior synthetic shellac from the well-known, but exceedingly refractory, reactions between phenol and formaldehyde. Again his approach was entirely realistic. He knew that we were importing between 40 and 65 million pounds of shellac each year from India. He realized the advantages and drawbacks of this raw material of the best varnishes. He knew that since 1871, when the great Adolf von Baeyer first investigated the reactions between phenol and various aldehydes, many chemists had gummed up their apparatus with the hard, tarlike, infusible, insoluble substances produced by these reactions and had consigned them to the laboratory slop jar. In fact, his work began with a literature search during which he painstakingly repeated all the experiments of his forerunners. Then he tried all sorts of solvents upon each of the unpromising

gunks resulting from these reactions. He learned what would not work; there was no hint as to what would. But he was not discouraged.

He began again and in place of formaldehyde he tried many other aldehydes. All reacted with phenol more or less violently and he got some suggestive variations. He began adding different quantities of various acids and alkalies. The former kept his messy products soft. The bases rendered them harder and reduced foaming during the reaction so that the product he obtained was less like a hard, dirty sponge. But he found nothing even close to the shellac he sought.

Suddenly, one day, he thought that if these condensation products of his were so damnably tough and unreactive, why not make a virtue of this vice? Surely there were uses for such a chemically stubborn substance. He quit trying to make a shellac substitute and started to hunt for a resin which could be molded permanently into definite shapes.

With this fresh objective he reversed his former methods. Instead of trying to hold down the reactions he stepped them up by every chemical and physical means. He tried various chemical accelerators. Instead of cooling, he applied heat. He combined heat with pressure; pumped air into an autoclave and raised the temperature to 200°C. Instead of the usual tarry mass he obtained a clear liquid that promptly solidified. He turned the autoclave over and out plopped a clear, hard hemisphere, its surface engraved with a perfect reproduction of the seams and boltheads that fastened the retort together. He examined the new material, eagerly, critically. It looked like amber, but was much harder. He could not dissolve it. He cut it with a knife, and so surmised it could be machined. It did not change its shape when heated or pressed. It did not absorb water, nor did it conduct electricity.

For two years longer the inventor of Bakelite worked with this new resinlike material. He perfected a two-stage production process and produced three distinct types for different purposes, one of them as a shellac substitute. He learned how to use this unusual substance; molding it, casting it, machining it, testing it to uncover its limitations and find its possibilities. He took out over 400 patents, covering every stage and variation of its production and many

of its broader applications. It was five years after he began these researches before he announced Bakelite to the world at a memorable meeting in the Chemists' Club, New York, on February 15, 1909.

As in the case of Velox, he exploited Bakelite himself. "At the beginning," he confessed, "I had the erroneous idea that almost anyone would be able to make the new material . . . that it would simplify matters if I issued licenses on a royalty plan for the use of my patents without going myself into the trouble of any manufacturing work." It took him some time to prove that the safe and proper way was to manufacture a semifinished product, ready for use in its final applications.

Thus Dr. Baekeland not only opened up an entirely new field in synthetic plastics, but his General Bakelite Company created the pattern upon which the new industry was to function. As in the case of most successful patents, there were infringement suits, which Baekeland always won, and in 1922 he combined with two of his litigation rivals, the Condensite Company and Redmanol Chemical Products Company, into the Bakelite Corporation, which five years before his death, became a unit of the Union Carbide & Carbon Corporation.

After the earlier merger, which brought him several former competitors who became valued associates, he devoted less and less time to the details of what had become Big Business. He spent more and more time on his estate in Florida, which ironically had been owned by that archenemy of modern science, William Jennings Bryan. There he grew exotic tropical plants and with his neighbor, Dr. David Fairchild, the botanical explorer, introduced several new fruits and flowers. His first hobby was automobiling. He owned one of the first cars, and in 1907 took his family motor-ing through Europe, a trip that furnished him material for a humorous travel book. In later years, he became an ardent yachtsman, sailing from the Hudson River to Miami and back, and exploring the little known islands of the Caribbean in his auxilliary yacht, the *Ion*.

In the midst of so many activities Baekeland was a prolific contributor to scientific and technical journals—52 papers published between 1903 and 1940—and he was constantly called upon as a

public speaker. Though he never quite lost his Flemish accent, his use of English was correct and dexterous, and some of his addresses are masterpieces of scientific exposition. He also found time to take an active part in professional societies, and he was chosen for important posts: president of the American Chemical Society, the American Institute of Chemical Engineers, the American Electrochemical Society, and the Chemists' Club. He was honorary professor of chemical engineering at Columbia University for many years, and this was no empty title.

He carried his many honors lightly, which was fortunate, for they would have overwhelmed a less sturdily modest man: honorary degrees from Brussels, Edinburgh, Pittsburgh, and Columbia, and the following medals: Nichols, 1909; John Scott, 1910; Willard Gibbs, 1913; Chandler, 1914; Perkin, 1916; Messel, 1938; Franklin, 1940. His native country bestowed upon him two orders, the Crown of Belgium and Leopold of Belgium, and from France, the Legion of Honor.

NOTES AND REFERENCES

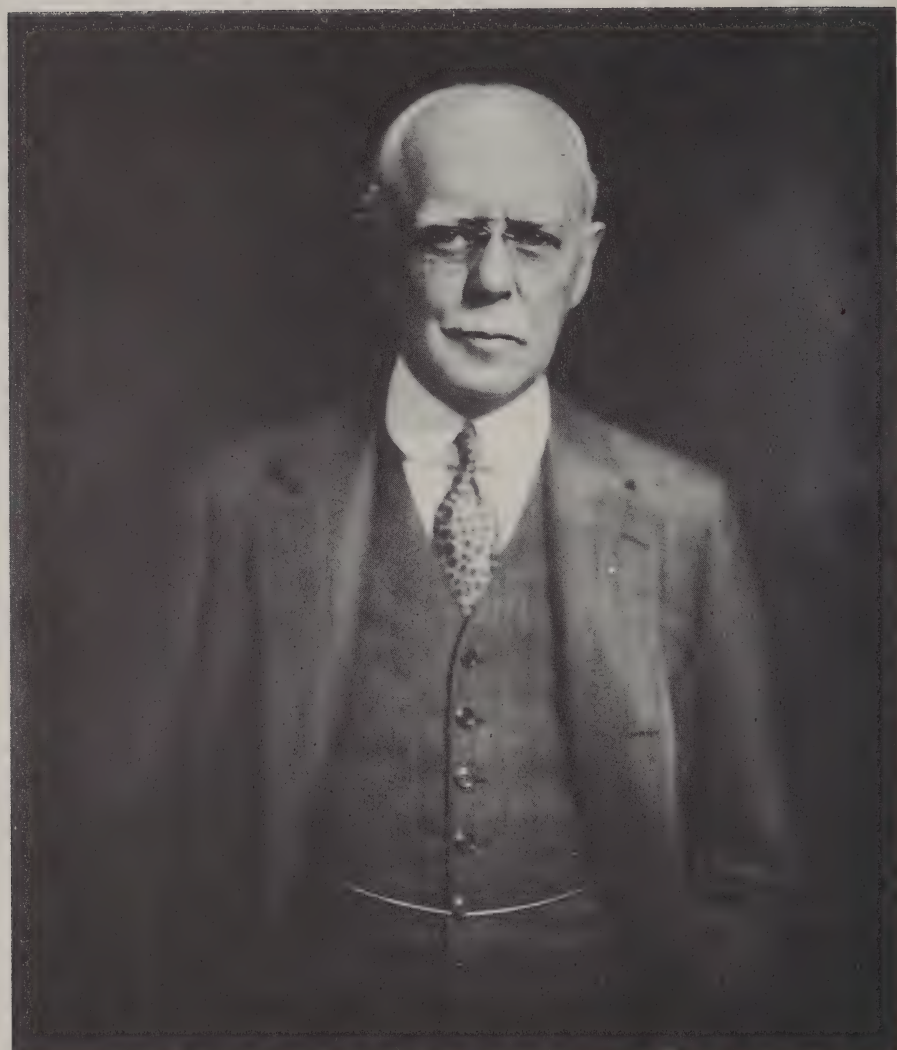
- Much of Baekeland's life work is ably recorded in his own papers and addresses, particularly his Perkin Medal acceptance (*Chem. Met. Eng.*, Feb. 1, 1916, p. 148) and there are a number of excellent biographical sketches, the most complete being H. V. Potter, *Chem. & Ind.*, Aug. 4 and 18, 1945, pp. 242, 251; but also Jas. Kendall, *Ibid.*, Jan. 29, 1949, p. 69; *Chem. Met. Eng.*, 40, 140 (1924); *Ind. Eng. Chem.*, 20, 1274 (1928); A. D. McFadyen, *Chem. Ind.*, 46, 614 (1940).
- For a lively account of the man and his work, see Maurice Holland, "Industrial Explorers," New York, Harper & Bros., 1928, pp. 92-112; see also *J. Frank. Inst.*, 230, 159 (1940); "Who Was Who," II, 36. Obit: *Chem. & Ind.*, Apr. 1, 1944, p. 134; *Nature*, Mar. 25, 1944, p. 369; and *N.Y. Times*, Feb. 24, 1944.

WILLIAMS HAYNES

.. 83 ..

Arthur Dehon Little

1863-1935



ARTHUR D. LITTLE was an outstanding leader among American consulting chemists during the first third of the present century. Because of arresting articles he wrote for the *Atlantic Monthly* and other magazines and several of his addresses which were reprinted and widely read, he was by far the best known to the general public of any of his contemporaries. He therefore occupied a position of great influence during an exciting, crucial period in the history of chemistry and chemical industry in the United States.

These were times of revolutionary change. No one recognized this more clearly than he; no one has so vividly pictured the great transformations of his day.

"When I opened a laboratory in Boston," he wrote in one of his best essays, *The Handwriting on the Wall*, "the street cars were drawn by horses, and I remember the clang of the first electric cars on Boylston Street and the consternation they caused among their equine competitors. From my window on Beacon Street 2000 bicycles an hour could be counted, where now automobiles pass. I have seen the fishtail burner supplanted by the Welsbach mantle, and the incandescent electric lamp develop from carbon to tungsten filaments and so to the white light of argon-filled bulbs. I remember the thrill when I first saw an airplane sweep at dusk across the disc of the rising full moon and soar to invisibility above."

In this delightful style he itemized the marvels he had witnessed—the phonograph; wireless telegraphy and the radio; x-rays; the rare gases found in the atmosphere and nitrogen snatched from the air; electrochemistry; catalysts and colloids—"all these great developments, so far-reaching in their influence upon industry, our mental outlook, and our entire social structure, have taken place within the easy recollection of a man still on the job."

Dr. Little was not content to paint pretty word pictures of the changing world in which he lived and worked. It is seldom given to a man to comprehend the causes and implications of stirring

contemporary events, and the more thrilling these events are, the greater are the chances that he will misinterpret them. The years during which Arthur D. Little was a chemical consultant were packed with many startling chemical developments. He was sensitive and imaginative and he responded acutely to these stimulants.

His insight and his foresight were both extraordinary. Living in the very eye of this tornado of chemical progress, he correctly identified new trends that were to have profound effects upon chemical science and technology, upon research and education, upon chemical production and consumption. He also greatly strengthened, and in a great measure directed, fresh influences to which we owe much chemical advance in both the scientific and commercial areas. He was at once prophet and promoter of chemical progress.

This altogether remarkable chemist was a rock-ribbed New Englander; a Bostonian, a very proper Bostonian. He was born within the walls of Fort Independence, one of the Revolutionary defenses of Boston Harbor, on December 15, 1863, the oldest of four sons of Thomas Jones and Amelia (Hixson) Little. His father, an artillery captain in the Civil War, had been severely wounded and ordered to this sinecure command for his recovery. He was the direct descendant of George Little who settled in Newbury, Massachusetts, about 1640.

When Arthur Little was quite young the family moved to Portland, Maine, and he received his earliest education in the public schools of that city. Later he attended the Berkley School in New York City. Young Arthur never dreamed of being a railway conductor or a fireman or even the ringmaster of a circus; when twelve years old he determined to be a chemist. Beguiled by a schoolmate's promise to show him some great experiments, he invested all his wealth, ten cents, in a piece of glass tubing, a bit of zinc, and five cents' worth of sulfuric acid. That afternoon the boys rigged up a hydrogen generator. It promptly blew up, luckily without damaging results, but he had witnessed the marvel of metal bubbling in acid and was completely converted to chemistry. No doubt, the noisy climax of this first experiment was a baptism never to be forgotten. A year later he had his own laboratory.

His absorption in chemistry did not prevent him from being a regular contributor to the school paper. It was apparently his chief extracurricular activity. At the Massachusetts Institute of Technology he became freshman editor, and eventually editor-in-chief, of *The Tech*, the college newspaper, and later, under his inspiration and guidance, the *Technology Review* became one of the best of the collegiate alumni journals.

Thus was the twig bent. Throughout his life, chemistry and literature were to be the mainsprings of Arthur D. Little's career.

Between 1881 and 1884 he was an undergraduate majoring in chemistry at M.I.T. He left before graduation to take a summer course in papermaking at Amherst and then became a chemist, later superintendent, of the Richmond Paper Company whose little 10-ton plant at Rumford, Rhode Island, was the first sulfite mill in America.

From this first job in the first American sulfite papermill, Little's chemical career was studded with pioneering accomplishments. The sulfite wood pulp process was theoretically right enough, but as installed at the Richmond mill it was all wrong in its engineering. It fell to the youthful superintendent to revise the apparatus and correct the layout—the classic task of “ironing the kinks out of a new process.” He did so, and incidentally devised the “Little Digester,” the subject of his first patent. This assignment accomplished, he was sent to New Bern, North Carolina, to install the sulfite process in another mill, and his place at Rumford was filled by Roger B. Griffin. The following year, 1886, these two aspiring young chemists formed the consulting firm of Griffin & Little.

They opened an office, eight by twelve feet, with an adjoining laboratory about twice as large, on the top floor of an antique building on Milk Street in Boston. Years later the distinguished Dr. Little used to speculate sadly upon how many clients refused to climb six stories when the decrepit elevator's dingy door bore the sign “Out of Order.” In those days the loss of a single client was a catastrophe. Although the consulting chemist was not highly esteemed and was very poorly paid, nevertheless this unpromising profession was definitely overcrowded in Boston. The new firm

had six hungry competitors. Each was anxious to analyze a sugar sample for seventy-five cents and delighted to make a sanitary report on water for five dollars.

Somehow the firm of Griffin & Little managed to scrabble along, as an old New Englander would say, and each year their income grew a little and their reputation a great deal. They did every routine analysis they could corral, but it was a few papermill clients who kept them from bankruptcy. Naturally they specialized in this field, and together they wrote "The Chemistry of Paper Making," for years the authoritative text on this subject. Gradually their practice turned more to engineering problems, to plant construction, to expert technical appraisals of processes and products. Twice they moved into bigger, better quarters. They built up a small staff of carefully chosen specialists. They even bought out a couple of their competitors. Then, in 1893, this successful partnership ended in a tragedy, a laboratory explosion in which Roger Griffin was killed.

Shocked as he was by his friend's death and crippled by the loss of an able partner to share the growing burdens of their expanding practice, Little decided to carry on alone. He did so for seven years till 1900. Then he formed a second partnership with Dr. William H. Walker, professor of chemical engineering at M.I.T. The firm of Little & Walker, Consulting Chemists and Engineers, continued for five years. Then the junior partner found the demands of business infringing so seriously upon his academic duties that he withdrew. In 1909, Arthur D. Little, Inc., Chemists, Engineers, and Managers, was organized. A precarious consulting practice had evolved into a great research institution.

Sometimes, in reviewing Arthur D. Little's many accomplishments, it is overlooked that he was the originator of this type of organization. The staff of experts he gathered together; the splendid building he built on Memorial Drive in Cambridge to house their activities; the multiplicity of services, ranging from pure science to market survey, which he and his associates offered to industry were bold innovations that have served as models for scores of similar institutions here and in foreign countries. All these were the natural evolution of his experience, a practical expression of ideals of research.

One graphic example will illustrate this. In the early days, when routine analyses were bread-and-butter jobs, one of the first regular clients was the old house of D. & L. Slade, spice millers who guarded their reputation for quality by having samples of their purchases tested microscopically and chemically for purity. It was a worthwhile precaution. Their raw materials came from Java and Ceylon, from Arabia and Tibet, from many out-of-the-way places; since the days of the Venetian and Florentine merchants, the trade in spices had been infamous for its sophistications. This close association continued many years, and the Little staff became adept in recognizing the cleverest adulterations; they devised better methods for their ready identification, they set up standards, and then logically they were called upon to do similar work for other foods.

Dr. Little's first and lasting chemical interest was cellulose. Papermaking by a new process was his initial chemical enterprise and this was the chief activity of his early years. He was granted patents on waxed and waterproofed papers and did much good work on the utilization of wood wastes. During this same period, he was introducing the chrome tanning process of Schultz and contributing advances to the electrolytic alkali process, to alcohol fermentation, casein products, the production of chlorates and hypochlorites; all of these were for the most part chemical pioneering.

In 1889 the Count de Chardonnet displayed his artificial silk, made from cellulose nitrate, at the Paris Exposition, three years after Griffin & Little opened their laboratory. They immediately reproduced his experiments. From the first, Little became a rayon enthusiast and while it was still a stiff, brittle, highly flammable fiber, he foretold that it would some day replace silk and even rival King Cotton. Cross & Bevan had hardly worked out their new viscose process before he obtained the American rights to their patents. Between 1893 and 1896 he offered these patents to J. P. Morgan, Frank Vanderlip, and Bernard Baruch, as well as to the leaders of our textile and paper industries. None of these astute gentlemen leaped to grasp this splendid opportunity. It was 1900 before the viscose process was firmly established in the United States. Then Courtaulds, the famous English textile firm, which had energetically taken up the viscose process and became

the world's largest maker of viscose rayon, bought two struggling experimental plants and organized the American Viscose Company.

All this time Little and his associates were eagerly experimenting with these new man-made fibers. The dangerous flammability of cellulose nitrate, which had inspired the discovery of viscose rayon, spurred other chemists to combine cellulose with other acids in the hope of getting a safer spinnable compound. Cellulose acetate had been reported in 1869, but it involved tricky reactions and high-cost reagents. The acetate fiber, although it had intriguing properties, was unanimously voted "commercially impractical." Little refused to accept this verdict. He could hardly have foreseen that twenty years in the future synthetic acetic anhydride would cut the price of this most costly ingredient by two thirds. However, he did sense the possibilities in fibers of different, distinctive characteristics. Thus he anticipated the blending of various synthetic and natural yarns which have given us a wealth of specialized fabrics from cobweblike sheers to noncrushable velvets.

Believing in cellulose acetate's future, Little continued these experiments over several years; by using, not cotton or filter paper, but the regenerated cellulose of the viscose process, he and his associates produced a number of marketable products. A thickish, clear sheet, three-feet square, was sold in competition with highly flammable celluloid. In January, 1903, they made the first commercial textile fiber. Two small companies were organized to make these acetate products, but they were only fitfully successful. Soon, however, their facilities and the know-how of the Little group were to render great service in helping supply a nonflammable dope to tauten and coat the canvas wings of fighting airplanes.

World War I came unexpectedly as a climactic end of the old era and the bright prelude to the new Chemical Age. Only one who lived through those experiences could sense the chilling anxieties roused by the famine of coal-tar dyes and medicines, of nitrate and potash, or feel the desperate urgency bred by the quick, great need for TNT, for phosgene, for salvarsan, for many chemicals not then made in America, and also for undreamed-of tons of such old stand-bys as sulfuric acid, caustic soda, chlorine, and benzene. Dr. Little was in the middle of many wartime activities, and his

brief article, "The Sinews of War," tells that dramatic story well. His own war work was chiefly with the new Chemical Warfare Service and the Signal Corps in the production of acetone, airplane dope, combat gases, gas-mask materials and smoke filters, flares, etc.

The war was a dramatic demonstration of two great lessons that Arthur D. Little had been teaching for years: (1) Chemicals are the key materials of our modern industrial civilization, and (2) research is the mainspring of our material progress and continued prosperity. The prophet of chemical progress was not now without honor in his own country. The promoter of chemical progress found before him a new world of opportunity.

In the postwar period Dr. Little continued to be a chemical pioneer. In his favorite field of cellulose chemistry he blazed a new path in the utilization of Southern pine in papermaking, thus opening the way to the great kraft paper and newsprint industries which have revolutionized the use of Southern timber resources and revitalized the economy of a half dozen states.

The vapor-phase cracking of petroleum evolved by Little and his organization was applied at Tiverton, Rhode Island. An experimental plant was built as a joint enterprise of the Barnsdall Corporation, the National Distillers Products Corporation, and the banking house of Blair & Company. Here were produced, on a commercial scale, high-test aviation gasoline, tertiary butyl-, isopropyl-, and other alcohols, and propylene and other unsaturated olefins. This operation was, in its technology and the products it produced, a forerunner of the petrochemical industry which has since loomed so large on the chemical horizon.

Arthur D. Little's many accomplishments won him merited honors: the Perkin Medal in 1931; honorary degrees from Pittsburgh, Manchester (England), Tufts, and Columbia. He was president of the American Chemical Society, 1912-14; the American Institute of Chemical Engineers, 1919; and the Society of Chemical Industry, 1928-29. This exceedingly rare "triple crown" was a fitting tribute alike to the man and the chemist.

Little was a handsome, clean-cut man with bushy eyebrows and ruddy complexion, slender and erect, of medium height, quick-moving with a brisk, heel-first step. His was a distinctive person-

ality, a chemist who collected Chinese porcelains, a somewhat austere New Englander with a twinkling eye and winning smile, a gentleman to the core who never lost the common touch. He was a meticulous man—careful in his dress and in his choice of words, discriminating in his tastes for literature and music, food and drink, and highly selective in his few close friendships. The impression that he lastingly created was one of secure dignity and captivating charm.

In his perceptive sketch of this distinguished, delightful gentleman Maurice Holland wrote: "If Arthur D. Little did nothing except talk, or write an occasional paper, he would still be contributing his share to the cause of scientific research."

That is true. His writings and speeches were potent influences in creating our new chemical epoch. In education he promoted the first chemical engineering courses based on unit processes. By precept and practice he raised the professional status of both chemists and engineers. He preached the gospel of research in practical terms by showing businessmen and bankers that a laboratory is as vital as an accounting room to the profitable life of an industrial company. He opened the eyes of thousands of Americans to the fact that their health, wealth, and safety depend vitally upon chemicals and that their future will be shaped by the results of continuing chemical progress. To read his essays and addresses, collected under the title of "The Handwriting on the Wall," is an illuminating and pleasurable experience. Here, too, he was meticulous. Often he labored a full day rewriting and polishing a single page. His speeches, so deftly delivered, were carefully written out and then carefully rehearsed.

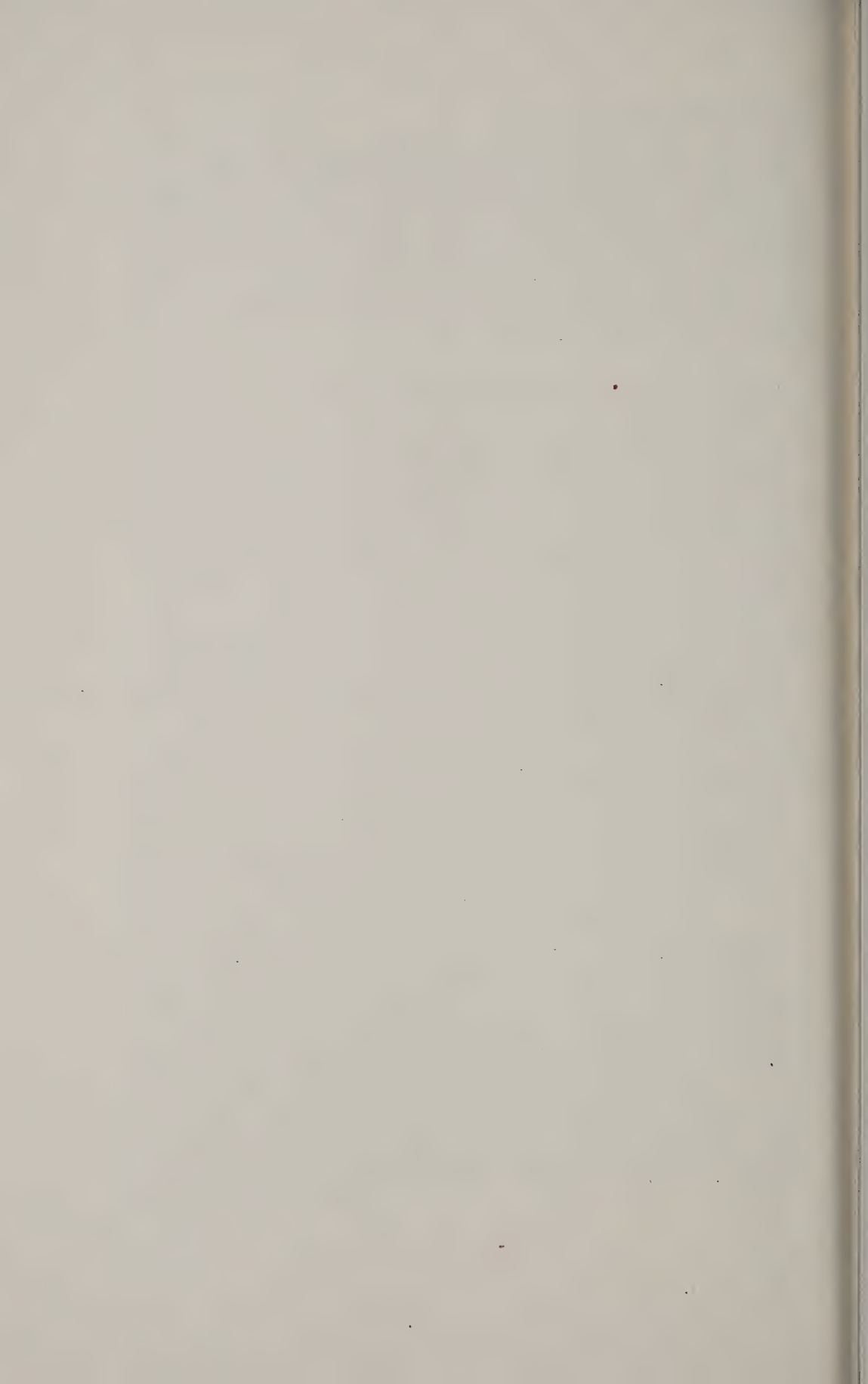
He lived his active life fully to the end, for he died suddenly of a heart attack at his summer home at Northeast Harbor, Maine, August 1, 1935, aged seventy-one. His widow survived him only two months. He and Henrietta Rogers Anthony were married January 22, 1901, and lived a life of peculiarly close and happy companionship. They had no children, but his nephew, Royal Little, grew up in their home. He recalls vividly the evenings they all spent together, reading aloud, listening to music, and above all, hearing Dr. Little review his working day in a manner as fascinating as the best of novels.

The majority stock of Arthur D. Little, Inc., was left to be administered by trustees, the profits to go to M.I.T., thus avoiding the intrusion of outside interests or a struggle among his old associates for control of the corporation. Later the Little staff purchased the estate stock and pooled their own shares in a retirement trust, a harmonious and profitable method of carrying on the aims and ideals of the founder.

NOTES AND REFERENCES

- Dr. Little's book, "The Handwriting on the Wall," Boston, 1928, is full of biographical facts and reveals much about the man himself. As often, the Perkin Medal presentation address, F. D. Keyes, *Ind. Eng. Chem.*, 23, 236 (1931), contains excellent material as do several biographical sketches: *Ibid.*, 20, 1395 (1928); Maurice Holland, *Industrial Explorers*, New York, 1928, pp. 149-69; Earl P. Stevenson, *Newcomen Soc. Address*, Boston, May 5, 1953; *Proc. Am. Acad. Arts & Sci.*, LXXI, 1937; "Who Was Who," I, 735; *Am. Bict. Biog.*, XXI, 500.
- For Little's part in American rayon development, Williams Haynes, "Cellulose: The Chemical That Grows," New York, Doubleday, 1953, pp. 125-47; for Arthur D. Little, Inc., *Ibid.*, *American Chemical Industry*, 6 vols., New York, Van Nostrand, 1945-54, VI, 249; for genealogy, C. T. Little, "Descendants of George Little," Boston, 1888.
- Obits: *Industrial Bull. of Arthur D. Little, Inc.*, Aug.-Sept. 1935; *Science*, Oct. 18, 1935; *Technology Rev.*, October 1935; *Boston Transcript*, Aug. 2, 1935; and N.Y. Times, Aug. 3, 1935.

WILLIAMS HAYNES



.. 84 ..

Walther Nernst

1864-1941



I ACCEPT with pleasure the invitation of the editors of this magazine to dedicate a few lines to the scientific personality of Dr. Walther Nernst, who died recently. For he was one of the most characteristic and most interesting scholars with whom I have been closely connected during my life. He did not miss any of the conferences on physics in Berlin, and his brief remarks gave evidence of a truly amazing scientific instinct combined both with a sovereign knowledge of an enormous volume of factual materials, which was always at his command, and with a rare mastery of the experimental methods and tricks in which he excelled. Although sometimes good-naturedly smiling at his childlike vanity and self-complacency, we all had for him not only a sincere admiration, but also a personal affection. So long as his egocentric weakness did not enter the picture, he exhibited an objectivity very rarely found, an infallible sense for the essential, and a genuine passion for knowledge of the deep interrelations of nature. But for such a passion his singularly creative productivity and his important influence on the scientific life of the first third of this century would not have been possible.

He ascended from Arrhenius, Ostwald, and van't Hoff, the last of a dynasty that based its investigations on thermodynamics, osmotic pressure, and ionic theory. Up to 1905 his work was essentially restricted to that range of ideas. His theoretical equipment was somewhat elementary, but he mastered it with a rare ingenuity. I refer, for instance, to the theory of electromotive powers in solutions of locally variable concentration, the theory of diminution of the solubility by adding a dissolved substance. During this period he invented the witty Null method of determining the dielectric constant of electrically conducting bodies by means of Wheatstone's bridge (alternating current, telephone as indicator, compensating capacity in comparison bridge branches).

This first productive period is largely concerned with improving the methodology and completing the exploration of a field the principles of which had already been known before Nernst. This

work led him gradually to a general problem which is characterized by the question: Is it possible to compute from the known energy of the conditions of a system, the useful work which is to be gained by its transition from one state into another? Nernst realized that a theoretical determination of the transition work A from the energy-difference U by means of equations of thermodynamics alone is not possible. There could be inferred from thermodynamics that, at absolute zero, the temperature of the quantities A and U must be equal. But one could not derive A from U for any arbitrary temperatures, even if the energy-values or differences in U were known for all conditions. This computation was not possible until there was introduced, with regard to the reaction of these quantities under low temperatures, an assumption which appeared obvious because of its simplicity. This assumption is simply that A becomes temperature-independent under low temperatures. The introduction of this assumption as a hypothesis (third main principle of the theory of heat) is Nernst's greatest contribution to theoretical science. Planck found later a solution which is theoretically more satisfactory; namely, the entropy disappears at absolute zero temperature.

From the standpoint of the older ideas on heat, this third main principle required very strange reactions of bodies under low temperatures. To pass upon the correctness of this principle, the methods of calorimetry under low temperatures had to be greatly improved. The calorimetry of high temperatures also owes to Nernst considerable progress. Through all these investigations, as well as through many stimulating suggestions with which his untiring inventive genius supplied experimenters in his field, he promoted the research work of his generation most effectively. The beginnings of the quantum theory were assisted by the important results of those caloric investigations, and this especially before Bohr's theory of the atom made spectroscopy the most important experimental field. Nernst's standard work, "Theoretical Chemistry," offers, not only to the student but also to the scholar, an abundance of stimulating ideas; it is theoretically elementary, but clever, vivid, and full of intimations of manifold interrelations. It truly reflects his intellectual characteristics.

Nernst was not a one-sided scholar. His sound common sense

engaged successfully in all fields of practical life, and every conversation with him brought something interesting to light. What distinguished him from almost all his fellow countrymen was his remarkable freedom from prejudices. He was neither a nationalist nor a militarist. He judged things and people almost exclusively by their direct success, not by a social or ethical ideal. This was a consequence of his freedom from prejudices. At the same time he was interested in literature and had such a sense of humor as is very seldom found with men who carry so heavy a load of work. He was an original personality; I have never met any one who resembled him in any essential way.

BIOGRAPHICAL NOTE

Walter Nernst was born on June 25, 1864, in Briesen (West Prussia). He graduated from the gymnasium as *primus omnium* (1883) and passed his examination for the doctor's degree *summa cum laude* (1887). In between he had studied physics at several universities, and he continued to change the place of his subsequent research work until Göttingen captured him for a long period, from 1890 to 1905. Then he became the successor of Hans Landolt in Berlin's Second Chemical Institute which Nernst soon converted into a physicochemical institute and which he directed until 1922. For two years he presided over the Physikalisch-Technische Reichsanstalt, and from 1924 to 1933 he directed the institute of experimental physics at the University.

In 1893, a year after he was married, he published a textbook with the translated title: "Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics." This title characterizes not only the content of the book but also the main line of Nernst's lifework. The thermodynamics of chemical reactions, considered from the viewpoint developed by Avogadro, led Nernst to several new theoretical concepts. To prove them by experiments he constructed several ingenious practical devices.

In his theory of electrochemical processes, he considers the metallic electrodes as a reservoir of ions. They have a tendency for electrolytical dissolution which has typically different values for different metals. When these ions enter into the solution, they

encounter, or they create, a pressure in the reverse direction. The example of gas behavior served here as well as it did in van't Hoff's theories of osmotic pressure. Nernst amplified these theories by stating the analog of "ideal solids" to the ideal gases.

Much wider was the range of his thermodynamic theorem. Definitions of the first and the second law of thermodynamics state that no *perpetuum mobile* of the first or second kind is possible. In analogy, Nernst expressed his theorem in the words: "It is not possible to build a caloric machine which will reduce the temperature of a substance to absolute zero."

Old rules, like that found by Trouton for the connection between boiling points and heats of vaporization, now appeared as simple consequences from Nernst's third law of thermodynamics.

From his electrochemical work Nernst derived new views of hydrogen in metallic compounds. When lithium hydride is electrolyzed in molten condition, hydrogen appears at the anode, like a halogen.

Two of his technical inventions attracted much attention but did not become widely accepted. One was the Nernst lamp, a ceramic rod which was preheated by an auxiliary current to a temperature of about 2200° C. at which it becomes a highly effective converter of electrical energy into light. The other was an electronic piano in which the player regulated the source of electrical energy which excited the strings to vibration. Nernst had no musical inclinations or abilities—somewhat astonishing in view of the frequent connection between musical and mathematical genius.

GENERAL REFERENCES

Max Bodenstein, "Walther Nernst," *Ber. deut. chem. Ges.*, 75 A, 79 (1942).

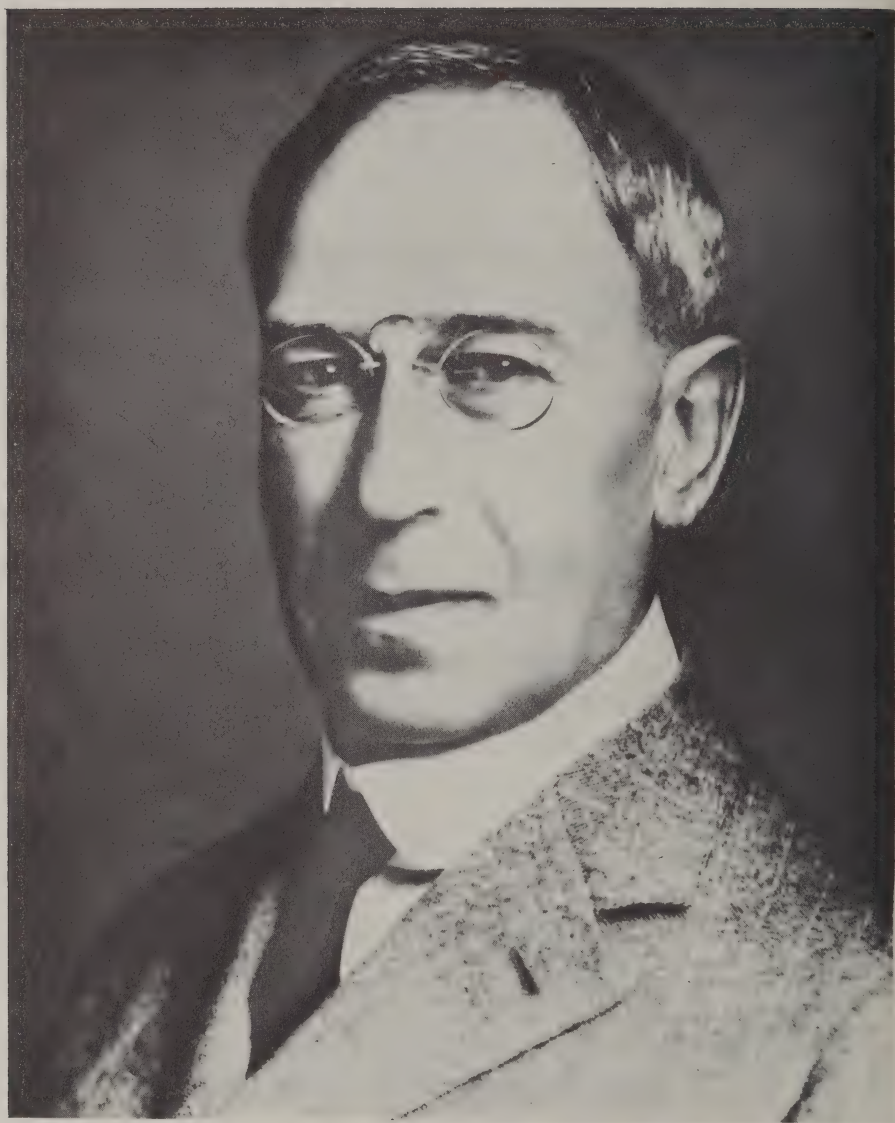
From: *Scientific Monthly*, February 1942, p. 195, with the biographical note by Eduard Farber.

ALBERT EINSTEIN

.. 85 ..

Moses Gomberg

1866-1947



THE death of Moses Gomberg on February 12, 1947, brought to a close the career of a brilliant scientist who had won recognition as one of the world's leading authorities in organic chemistry. He was born on February 8, 1866, in the small town of Elizabetgrad, Russia, the son of George and Marie Resnikoff Gomberg. From 1878 to 1884 he was a student in the Nicolau Gymnasium of his native town. In the latter year his father was accused of anti-Czarist activities and was forced to flee with his family, and his estate was confiscated. With help from friends they were able to go to Chicago where for a time hardship became their lot. Neither father nor son had a knowledge of English and they both worked in Chicago at whatever occupation they could find, and for a time at least in the stockyards. The son, however, with indomitable energy earned the means to complete his high school course and to enter the University of Michigan from which he was graduated in 1890 with the degree of Bachelor of Science. An assistantship enabled him to continue in graduate work, and two years later he received the degree of Master of Science. He took his doctorate in 1894 with a thesis on the reactions of caffeine, under Professor A. B. Prescott.

Even before his appointment as instructor in 1893, he was planning to study abroad and in order to earn the necessary funds, he spent his spare time in analyzing materials for his numerous clients. His versatility is shown by the fact that his work included the analysis of minerals, water, fats and oils, foods, patent medicines, and drugs. He was also employed frequently as an expert witness in toxicology cases, and he thoroughly enjoyed matching wits with the opposing lawyers. However, he was greatly disturbed by the necessity of doing this type of work because it interfered with the progress of his research, and he dropped it as soon as possible. Thereafter he refused steadfastly to accept consulting work of any kind.

A leave of absence from 1896 to 1897 permitted a year of study in Germany and he decided to spend two terms in Baeyer's labora-

tory in Munich. Thiele suggested a problem involving the preparation of isonitramino- and nitrosoisobutyric acid, and this work resulted in a 22 page paper in Liebig's *Annalen*.

The third term of the year was spent in Victor Meyer's laboratory in Heidelberg. In discussing the choice of a problem, Gomberg said that he wanted to prepare tetraphenylmethane. Meyer, as well as other chemists, had been interested in the synthesis of this compound and had tried various methods but without success. Consequently, Meyer suggested other more suitable problems but Gomberg was determined to go ahead, and his confidence was well deserved for he was successful in his attempt. His method consisted in oxidizing triphenylmethanehydrazobenzene to the corresponding azo compound and heating the latter to 110 to 120° C. However, the yield was very poor, only 2 to 5 per cent.

His next step, when he returned to the University of Michigan, was to investigate the preparation of the related hexaphenylethane in the hope of obtaining this completely phenylated hydrocarbon in greater yield. Accordingly, triphenylchloromethane in benzene was treated with sodium but without appreciable action. However, when molecular silver was used, a colorless compound precipitated, which was assumed to be hexaphenylethane. An elementary analysis gave low values for the percentage of both carbon and hydrogen. When further analyses gave the same result, it was concluded that the compound contained oxygen; and, after the silver had been shown to be free of oxide, it was suspected that oxygen of the air was oxidizing the initially formed hydrocarbon. By working in the absence of air, Gomberg obtained a hydrocarbon which was extremely unsaturated in its behavior. In benzene solution it absorbed chlorine, bromine, and iodine, and when exposed to air a stable peroxide was formed. In view of these remarkable properties, in his first paper (1900) on the hydrocarbon, Gomberg wrote, "The experimental evidence . . . forces me to the conclusion that we have to deal here with a free radical, triphenylmethyl, $(C_6H_5)_3C$. On this assumption alone do the results described above become intelligible and receive an adequate explanation." Following the publication of this paper, other chemists¹ immediately became interested in his hydrocarbon, and confirmed its striking properties. Moreover, it was shown that triphenylmethyl was but one of a large group of similar triarylmethyls.

However, for almost ten years, the existence of free radicals was questioned. Although the chemical evidence in favor of the trivalency of carbon was convincing, molecular weight determinations of the hydrocarbon indicated a value practically double that of the free radical. Consequently, a great deal of skepticism was shown, for there had been other somewhat similar cases involving radicals such as Gay-Lussac's cyanogen, Bunsen's cacodyl, and Frankland's and also Kolbe's alkyls. These had been described as free radicals but later were found to be dimolecular. It was assumed that Gomberg's hydrocarbon was just another instance of history repeating itself, and the concept of free radicals was ignored.

The situation in the period of 1900 to 1905 was confused by the fact that the new hydrocarbon was not regarded as hexaphenylethane because its properties were so different from what were expected. Furthermore, in 1902 Ullmann and Borsum had prepared a compound which was universally accepted as hexaphenylethane until Chichibabin showed two years later that it was *p*-benzohydriltetraphenylmethane,



In the meantime, various quinonoid structures had been suggested, but none of them proved satisfactory in explaining the unique properties of the Gomberg hydrocarbon. As all attempts to prepare a different hydrocarbon with the structure of hexaphenylethane failed, the majority of chemists began to look upon Gomberg's compound as hexaphenylethane, and considered it to be unstable, (i.e., reactive to iodine, oxygen, etc.) *per se*. Gomberg, however, remained unshaken in his belief in the existence of triphenylmethyl and time and again reiterated his faith in the concept of free radicals.

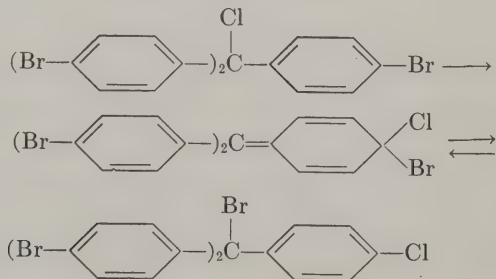
A study of other triarylmethyls hastened considerably the acceptance of the idea of free radicals, and an early suggestion (Flürscheim, 1905) that colorless hexaphenylethane dissociates in solution into colored free radicals, $\text{Ar}_3\text{C}-\text{CAr}_3 \rightleftharpoons 2\text{Ar}_3\text{C}$, was adopted. Under comparable conditions some radicals, like triphenylmethyl, remain only slightly unassociated, others are present in solution to a greater extent (20–80 per cent), while others like tri-*p*-biphenylmethyl (Schlenk) exist as free radicals even in the solid state.

Later, Wieland showed that tetraphenylhydrazine dissociates to give a free radical with divalent nitrogen, and other cases of free radicals with abnormal valences were reported. It was evident that Gomberg had opened an entirely new field in chemistry which was of extreme importance. This was further emphasized when Paneth demonstrated the transitory existence of the radicals ethyl and methyl, and it was soon shown that such transitory radicals are intermediate products in certain chemical reactions.

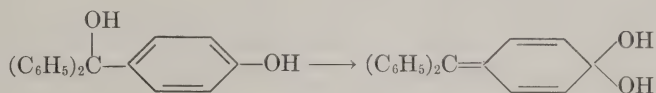
Another phase of Gomberg's work was concerned with the development of the quinonoid theory. Solutions of triphenylmethyl have an orange-yellow color, and Schmidlin found that there is both a colorless and a colored form present. In order to account for the two forms, Gomberg assumed that one of them must be quinonoid. In 1901, Gomberg and other investigators obtained double salts of triphenylchloromethane which were intensely colored, and Kehrman assigned a quinonoid structure to such compounds, e.g.,



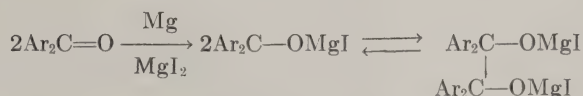
Baeyer vigorously opposed this view and claimed that the color was due to salt formation and could be explained on the basis of his theory of halochromism. In considering this problem, Gomberg reasoned that if there was a quinonoid form of *p,p',p''*-tribromotriphenylchloromethane in solution in liquid sulfur dioxide, a bromine atom would become labile and a shift of chlorine and bromine might be expected. To test this idea, he dissolved *p,p',p''*-tribromotriphenylchloromethane in liquid sulfur dioxide, and, after a few days allowed the sulfur dioxide to evaporate slowly. The resulting product contained 85 per cent of *p,p'*-dibromo-*p''*-chlorotriphenylbromomethane,



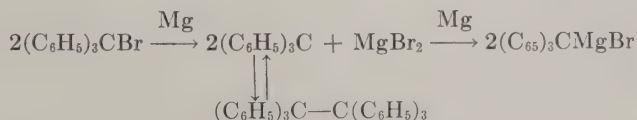
The shift of the chlorine atom and the bromine atom provided positive evidence in favor of the quinonoid theory. But in no case so far, had it been possible to isolate the two tautomeric forms of any triarylmethyl salt. However, Gomberg was able to isolate the benzenoid and the quinonoid form of *p*-hydroxytriphenylcarbinol in the crystalline state, thus helping to establish the quinonoid theory on a firm basis:



One of his last investigations was concerned with a study of the reducing action of the binary system $\text{Mg} + \text{MgI}_2$ on organic compounds in anhydrous ether and benzene. Gomberg postulated that the active reducing agent was magnesious iodide which was formed by interaction of the metal and its halide according to the following formulation: $\text{Mg} + \text{MgI}_2 \rightleftharpoons 2\text{MgI}$. This hypothesis served to explain the reduction of $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{N}=\text{N}$, and other unsaturated groups in compounds. By this new reducing agent aromatic ketones were reduced to pinacols in high yields through the intermediate formation of colored free radicals (analogs of sodium ketyls).



Aromatic aldehydes, acids and their alkyl esters were found to be converted into benzoin. In the preparation of the Grignard reagent from triphenylmethyl bromide and magnesium Gomberg showed that the first step is the quantitative formation of triphenylmethyl \rightleftharpoons hexaphenylethane. The Grignard reagent is produced in the second step by the reaction of the free radical with the mixture of magnesium and magnesium bromide,



The reaction is unique in that a Grignard reagent can be prepared from a hydrocarbon (hexaphenylethane).

Other investigations included the first synthesis of unsymmetrical tetraphenylethane and one of the first syntheses of pentaphenylethane, the preparation of benzyl ethers of carbohydrates, the synthesis and study of certain dyes, a study of the $(\text{ClO}_4)_x$ radical and the synthesis of biaryls by the diazo reaction (Gomberg reaction). However, an examination of his publications reveals that most of his life was devoted to the investigation of triarylmethyls and related compounds.

Professor Gomberg was a member of many learned societies: the American Philosophical Society; a fellow of the American Association for the Advancement of Science; the Franklin Institute; the National Academy of Sciences; the American Institute of Chemists; the Netherlands Chemical Society, of which he was an honorary member; and the American Chemical Society, of which he was president in 1931. His achievements were recognized by the award of various honors: he was the recipient of the Nichols Medal in 1914; of the Willard Gibbs Medal in 1925; and of the Chandler Medal in 1927. He received the degree of Doctor of Science from the University of Chicago in 1929, the same degree from the Brooklyn Polytechnic Institute in 1932, and the degree of Doctor of Laws from the University of Michigan in 1937. He would have been less than human had he not been pleased by these marks of distinction, but none of them ever changed the even tenor of his ways. All evidences of his attainments were received with modesty that was one of his characteristic traits. He never sought preferment, and all forms of academic advertising were alien to his soul.

During the First World War he joined the group of civilian chemists working on gas warfare under the direction of the Bureau of Mines, prior to the organization of the Chemical Warfare Service. His assignment was the preparation of mustard gas; and although this was abhorrent to his nature, he accepted it without hesitation. Ethylene chlorohydrin was the intermediate which was required, and the method which he developed was the first in this country for the commercial preparation of this important compound. This work was done in his laboratory in Ann Arbor. Later in 1918, he was commissioned as Major in the Ordnance Department, acting as an advisor in the manufacture of smokeless powder and high explosives. Except for the year of study in Germany, this

was the only break in his teaching career which extended over a period of forty-three years.

He was chairman of the department of chemistry from 1927 to 1936 when he retired. He stressed the necessity of a thorough basic training in all branches of chemistry with a minimum of specialization. He believed that teaching on the university level was impossible without research, and in regard to Ph.D. candidates he felt that the emphasis should be placed on the training of the candidate and not on the issuance of a publication. He had strong convictions on such matters and was not adverse to expressing them, but he never spoke with harshness or with intent to hurt. In his contacts with students, he was sympathetic, gave generously of his time, and was always ready to offer friendly advice.

Gifted with a remarkable memory, he presented his lectures with the full use of a wealth of historical material and so vividly that they left an indelible imprint on his students. A great teacher and scholar, he inspired his students by his methods and ideals, and his colleagues by the vigor and clarity of his mind. To this greatness, he added an innate kindness and unassuming modesty that endeared him to all.

He never married and lived quietly and happily with his younger sister.

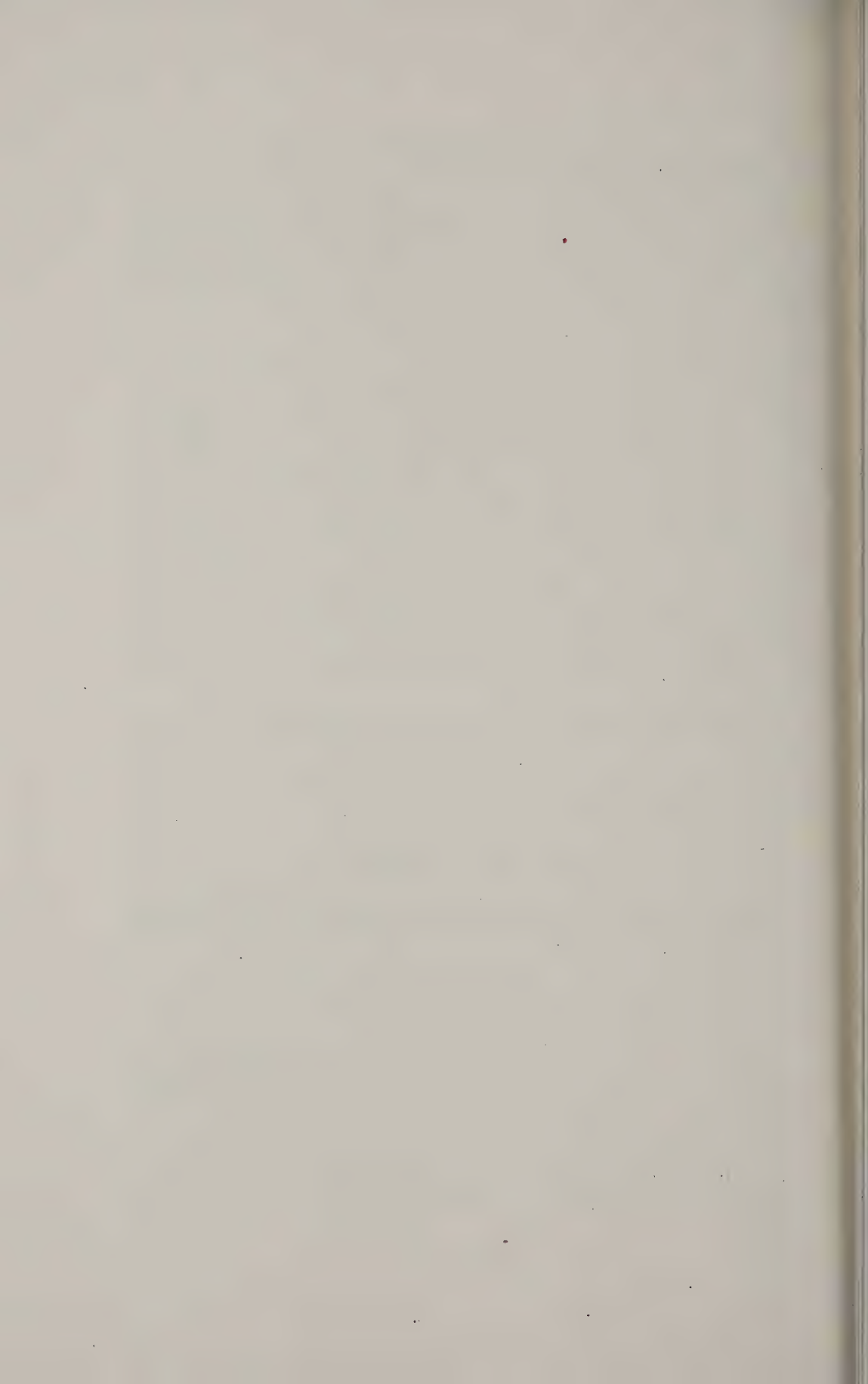
He was a great scientist, a wise counselor, and a loyal friend whose memory will long remain a living force.

NOTES AND REFERENCES

¹ Among the chemists who participated in the discussion of the structure of the unusual hydrocarbon were Baeyer, Markownikov, Thiele, Flürscheim, Schmidlin, Werner, Hantzsch, and Wieland.

From: *J. Am. Chem. Soc.*, 69, 2921 (1948).

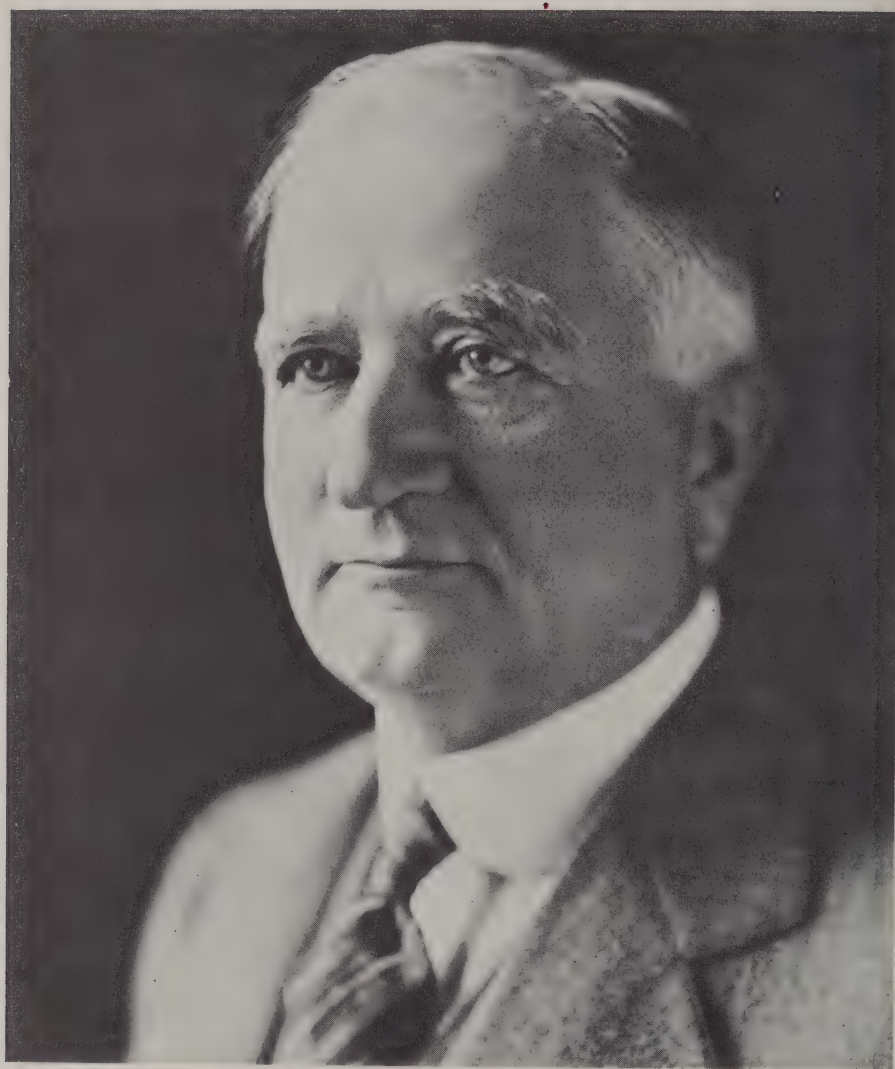
C. S. SCHOEPFLE
W. E. BACHMANN



.. 86 ..

Herbert Henry Dow

1866-1930



HERBERT H. DOW'S associates in The Dow Chemical Company delighted to argue whether he was greatest as a chemist, a chemical engineer, or a businessman. At times their debates waxed hot. Such a separation of his capabilities was, of course, impossible and apt to become invidious, but this hearty partisanship among his colleagues was full of meaning.

Their endless arguments were pure hero worship, a sublimation of the affection and admiration Herbert Dow inspired in everyone who came in close contact with him. At the time of his death, one of the chemical trade papers truly called him "the idol of Midland, Michigan." The almost idolatrous esteem of this great man and his many-sided accomplishments was, and still is, his finest monument. It explains not only his continuing influence upon the company he founded, but also the niche he occupies in the annals of the American chemical industry.

Very specially Dr. Dow personified the epochal changes transpiring in the chemical field during the first quarter of the present century, the years of his active career as a chemical manufacturer. He was typical of the transformation of the individual proprietor into the corporation executive which happened quite generally throughout the chemical industry at this time. Simultaneously and in a fashion just as typical of the whole industry, The Dow Chemical Company grew from the modest producer of two simple chemicals, bleaching powder and bromine, into a gigantic, fully integrated mass producer of over 500 chemicals, ranging from chlorine and caustic soda to bromindigo and the polymers of dichlorodiethylformal and alkali polysulfides. Historically, he was a perfect personal exemplar of the exciting, revolutionary period that saw the birth of the Chemical Age of our American economy.

Herbert Henry Dow was born February 26, 1866, at Belleville, Ontario. His father, Joseph Dow, a real Yankee tinkerer of the old school, had been sent to Canada to establish a branch sewing machine factory for his employers, but he returned to Birmingham, Connecticut (now part of Derby), before his son was three months

old. The Dows are an old New England family, established when Henry Dow came from England to the Massachusetts Bay Colony in 1637. Herbert's mother, Sarah Bunnell, was also a descendant of the first Massachusetts settlers.

Although the family moved to Cleveland, Ohio, when he was twelve. Herbert Dow bore throughout his life the strong impress of this ancestry and his strict upbringing. He had the Puritan virtues: he was honest, hard-working, thrifty, God-fearing. He was also blessed—or cursed—with a New England conscience. One of his oldest associates, Thomas Griswold, wrote of him that "He seemed unconsciously to practice all the rules of personal efficiency laid down by the teachers. He had no interest in avocations or recreations as such, but only if he could turn them into an asset of some sort." His methods and his thinking both reflected his New England background; he was saved from Puritan austerity and priggishness by his magnanimous spirit and a lively sense of humor.

It is remembered that as a boy he was an inveterate trader and also that he usually got the best of the bargain. He was also a great collector—birds' nests and eggs, butterflies, minerals, arrowheads, postage stamps—and when his interest changed, he sold or swapped his old collection to start his new hobby. At ten years of age he earned the money for his railway fare to the Philadelphia Centennial Exposition, which he visited with his father and where he was lastingly impressed by the huge Corliss steam engine.

Inspired by an article on ostrich farming in Australia in "The Youth's Companion," he became a true industrial pioneer by manufacturing one of the first incubators. His initial set of eggs failed to hatch because the kerosene lamp, which furnished the heat, did not maintain an even temperature. He solved this by inventing a practical heat-control apparatus, and the apex of his success was the sale of an incubator to a rancher in California for \$100. This success attracted imitators and he met their cut-price competition by advertising a set of blueprints with full directions to "build it cheaper yourself." This juvenile business venture embodied the invention of one of the earliest automatic control instruments and a new philosophy of sales, both prophetic of his activities as a chemical industrialist.

In Cleveland, where Joseph Dow was master mechanic of the Chisholm Steel Shovel Works, the family lived in a big house with spacious grounds at the corner of Superior and Cass Avenues, and Herbert with a chum went into market-gardening, selling vegetables to the neighboring stores. His father taught in the Sunday school and he sang in the choir and organized a quartet which gave many concerts to raise church funds: more forecasts of the future.

Young Dow dreamed of becoming an architect, but he won a scholarship at the Cast School of Applied Science, which offered no course in architecture, so for some unknown reason he elected to specialize in chemistry. The Case faculty was a group of driving, inspiring enthusiasts; the curriculum was preeminently practical; in the laboratories students were expected to carry on original research in applied chemistry. In this atmosphere Herbert Dow blossomed. He speeded up his regular course assignments to find more time for chemical hobbies of his own. In his junior year he became interested in lithium, then a rare and costly metal which had become a medical fad, and in the laboratory he recovered several samples, along with bromine, from Ohio brines.

During the winter term of 1887 to '88 he went to work on his graduation thesis, "The Chemical Uses of Fuel in Boilers," by conscientiously collecting samples of petroleum and natural gas from wells near Cleveland. At one operation he visited, the boss driller called his attention to the brine from this well.

"Just taste it," he said, "it's the bitterest brine I ever struck."

"Why?" was the question that popped into the young chemist's head and he determined to find out. Analysis revealed an exceptionally high content of both lithium and bromine.

Dow finished his thesis on boiler fuels, but that very acrid brine haunted him. He knew oil was selling for a dollar a barrel, he had figured out there was three dollars' worth of lithium in a barrel of that brine. His commercial instinct, always keen and always stimulated by his chemical investigations, told him that this particular well was more valuable for its wasted by-product than for the oil that was being sold with difficulty in an over-supplied market. At the same time his very sound business sense told him that the bromine content of the brine was even more important industrially than the higher-priced, but less-demanded, rare metal.

Here was the tiny acorn that was to grow into the mighty Dow Chemical oak, and young Dow must have sensed intuitively that he had hold of a good idea. He accepted a poorly paid position with the high-sounding title of professor of chemistry and toxicology at the Huron Street Hospital College of Medicine because it gave him a laboratory and an assistant so that he might continue his study of native brines. It was a task that was to engage his best attention the rest of his life.

Recovery of bromine, a heavy, very volatile, brownish-red liquid, is one of the older American chemical enterprises. David Alter started it during the early 1840's from brine found in Pennsylvania oil wells. The process was simple, but needed close attention if a pure product was wanted. First, the brine was evaporated till the salt (sodium chloride) crystallized out. Then, the concentrated liquor, called *bittern*, was treated with chlorine or either hydrochloric or sulfuric acid, which, reacting with the potassium and calcium bromides, freed the bromine that was driven off by heating and collected under water. The business settled in the Pomeroy district along the Ohio Valley and in the Kanawha Valley of West Virginia, where there was the favorable economic combination of a bromine-rich brine and abundant fuel. The demand was not big, but it was increased, especially during the Civil War, by the discovery of dry-plate photography and the medical vogue for bromides, the first tranquilizer drugs. Shortly afterward bromine recovered as a by-product from the famous German Stassfurt potash deposits appeared on the market and the price dropped from \$10 to \$4.50 a pound. The American industry shrank to a few plants operating only where waste wood from lumbering operations or local natural gas made fuel costs very low.

Dow combed this situation, he read and he experimented. He went scouting to find brine with the highest bromine content and found it at Canton, Ohio, and Midland, Michigan. Among the family archives are expense accounts of these trips. One four-day, triangular journey from Cleveland to Toledo to Findlay cost \$7.80, with one hotel at \$1 and another at \$.70 a day, which included meals, and "shave and shine" for \$.20.

He convinced himself that bromine could be freed from raw, cold brine and recovered by blowing it out of the liquid. By thus

practically eliminating fuel costs he believed he could make the cheapest bromine in the world.

His idea was tried out in 1889 at Canton, Ohio, by the woefully underfinanced Canton Chemical Company. The processes worked: he did liberate bromine from cold brine by sulfuric acid; he did collect the bromine by dribbling the treated brine over a series of burlap sheets spread above a fan; he did make ferric bromide by passing the liquid bromine through iron scrap. The company failed because of "mechanical troubles" caused by lack of capital. A critical point was the pump, a museum piece that simply could not raise enough brine from a 1000-foot well to produce enough bromine to make the operation profitable. Within the year his backers withdrew and Dow returned to Cleveland.

He had learned valuable lessons. One might improvise buildings and certain apparatus, but mechanical and electrical equipment should not be bought from the junk dealer. It was many years before he again tried to pump from so deep a well, and this was one reason why he moved to Midland where the bromine-rich brine was closer to the surface.

During the autumn of 1890 Dow's second bromine venture was launched in the Midland Chemical Company, a partnership in which he supplied the knowledge and work and J. H. Osborn furnished the money. They rented a brine well near the end of Midland's Main Street and an unused barn from an adjacent flour mill. Here he developed his second revolutionary idea, the separation of bromine from raw brine, not by chemicals, but by an electric current. His notebook dates the first commercial operation of any electrochemical process in the United States:

Tues., Dec. 9: Tried the dynamo.

Jan. 2, 1891: Started pump at 7 a.m. On hand \$2.26.

Jan. 4: Bromide of iron started running for the first time this morning. Ran power 24 hrs.

The first "kink" in the electrolytic process was exact control of the current; if too weak, all the bromine was not liberated; if too strong, chlorine also came over, a serious contamination for medicinal uses. It took a couple of years to get good working practices and

several more to achieve his goal of accurate automatic control. Because of a larger demand, he switched his end product from ferric to potassium bromide, using potashes (crude potassium carbonate) leached from wood ashes bought from nearby sawmills. This new raw material introduced a number of undesirable contaminants, and by cut-and-try experiments he learned that, being mostly organic substances, they could be driven off by calcining the bromide to red heat. Still the product, although as good as any on the market, was not quite up to U.S.P. standards.

Herbert Dow now turned salesman. After two futile calls in Cleveland, he went to Rosengarten & Sons in Philadelphia.

"We buy only from firms of the highest reputation," they told him rather brutally, "and do not, for our own reputation's sake, dare buy from a little one-horse concern in Michigan." However, in the end, he sold two barrels, "as a trial," at \$.17 a pound, exactly half the market price.

Returning to Midland, he inspected two barrels and found them full of black specks. For two days he and his bride— Grace Ball, a Midland girl, also of New England ancestry—picked over those two barrels to remove every speck and imperfectly formed crystal. The shipment was made, C.O.D., but no check was forthcoming. An anxious week later, came a letter saying that examination showed the bromide did not meet U.S.P. standards and asking what price concession would he be willing to make.

"That letter," so he wrote years later, "sent my heart down into my boots. We needed the money very much. . . . Fortunately for the future success of the organization there happened to be a business man in our office who volunteered to answer the letter. In substance our reply was as follows: 'We are in receipt of your letter of recent date. If the goods are not satisfactory, please return them'."

Their reply was a check in full payment of the account. Meantime the Midland Chemical Company struggled for lack of cash. Before offering potassium bromide they had sold bromine as a disinfectant and antiseptic and a mixture of alkali bromides as "mining salt" for the extraction of gold ores. But again the output of a makeshift plant hamstrung profitable operations. To provide additional capital two more partners were taken in, and then, on

August 17, 1892, the Midland Chemical Company was incorporated with an authorized capital of \$100,000, only about \$10,000 of which was paid in. Young Dow evidently lost financial control, for he was elected a director, but not an officer, of the corporation which hired him as manager. Another \$10,000 was raised by a bank loan in Cleveland; land was bought at the other end of town; the barn was deserted for a new-built plant. Here the centers of interest were a big, new 50-kilowatt generator, a giant of its day, and the first Dow electrolytic cell, a long, troughlike apparatus with carbon electrodes piercing the wooden partitions which divided it into six smaller cells.

In 1894, the year after the historic sale to Rosengarten, the Midland Chemical Company made a profit of \$11,781.78. The following year it began paying dividends at the rate of 2% monthly.

Herbert Dow had become interested in chlorine. It was much more plentiful than bromine in the brine and it had many more chemical possibilities. He hated to see it going to waste, for he knew it could be recovered electrolytically and he wanted to convert it into bleaching powder (calcium hypochlorite), then imported from England, for which the demand was growing rapidly.

Very humanly, his directors' response to this proposal was, "Let's make a little money before we squander it on more experiments." That was the correct business philosophy of the Gay Nineties. But they did give him permission to build a pilot plant on their property with the understanding that any patents he developed belonged to the corporation.

Dow went along with his plan, but two hours after the current was switched on his little new plant was demolished by an explosion of the hydrogen which was also released by the electrolytic dissociation of the sodium chloride. Fortunately nobody was hurt, but the bromine plant was damaged, and the special meeting of the directors turned into an indignation meeting. Dow did not resign as a director, but he moved 300 miles away from Midland to Navarre, Ohio.

Here, behind an 8-foot wooden fence he proved within a few months that he could liberate chlorine from a solution of salt in water by electrolysis without an explosion. All of his directors had not deserted him, and the faithful Osborn, with two of the Case

faculty, Cady Staley, president, and Albert W. Smith, professor of chemistry, and James T. Pardee, a classmate, organized the Dow Process Company to exploit this chlorine project. Back in Midland Dow built across the street from the bromine plant and bought its debromized brine as his raw material.

Shortly afterward this new partnership was incorporated as The Dow Chemical Company and its financial resources were strengthened by the sale of stock to 57 individuals. Three years later, Dow Chemical took over the Midland Chemical plant and bromine process. In 1902 a subsidiary was formed, Midland Chemical II, to manufacture chloroform from carbon tetrachloride, a process evolved by Professor Smith.

The path ahead was steep and stony, but the goal, if far away, was now clearly visible. For the first ten years technical advances were greater than financial returns. That was Dr. Dow's way, a fixed policy expressing a typically chemical philosophy of industry:

Here at Midland our job is to make chemicals out of our brine. I want to see us extract every chemical opportunity out of our raw material. . . . But I am not at all interested in making anything, except to salvage a by-product or a waste, that we cannot make cheaper and better than anyone else is making it.

At the time Dr. Dow was awarded the Perkin Medal, in 1930, Edwin O. Barstow, one of his oldest associates, summarized how these ideas were translated into action:

Carbon bisulfide, with chlorine, gives carbon tetrachloride; sulfur chloride and impure sulfur as by-products.

The by-product sulfur is used in the manufacture of limesulfur, a fungicide spray material, and also for the manufacture of epsom salt.

Carbon tetrachloride, treated with iron borings and water, gives chloroform and by-products of ferrous chloride and ferrous hydrate.

By-product ferrous chloride and ferrous hydrate, treated with chlorine and hydrochloric acid, give ferric chloride.

Benzene, treated with chlorine, gives monochlorobenzene with by-product hydrochloric acid.

Chlorobenzene with caustic soda solution at high temperatures

and high pressures gives sodium phenate solution, and this with by-product hydrochloric acid gives phenol.

Phenol, combined with caustic soda and carbon dioxide, gives salicylic acid, and from this we manufacture a full line of salicylates, including methyl salicylate, salol, and aspirin.

And so on and on, juggling their basic elements, chlorine and bromine, sodium, calcium, and magnesium, the list of Dow products has grown and grown.

Herbert Dow's career after 1900 was meshed with the development of The Dow Chemical Company. Although this is no place for a company history, nevertheless a few high points are too illustrative of the man to be omitted from his biography.

In the very early days Dow had to fight and win two costly price wars with powerful foreign competitors in bleach and bromine. The bleach victory was won, as it were, by default, for the Leblanc process employed by the United Alkali Company, Ltd., was already obsolete. The war with the German bromine cartel was quite different.

Recovering bromine as by-product from the Stassfurt potash salts, the Bromkonvention dominated world trade and when Dow began exporting bromides to Europe they warned him to stop or else—. He kept right on and a year later the price of German bromides in New York was suddenly cut to \$.15, half of the Dow price. Dow immediately withdrew from the American market and began shipping every pound of his bromides to Germany and England, just underselling the cartel, which naturally had not cut prices in these territories. In their eagerness to crush this upstart the Germans cut their American price to \$.10. This was below Dow's cost, so he began buying their material, repackaging it, and shipping it abroad. The Konvention got into double trouble: their members quarreled as to who should supply this unprofitable market and their customers here began complaining about deliveries. It took nearly four years to convince the Germans they had best pocket their losses and withdraw with tarnished prestige.

About this time, 1909, Dow made a serious decision that illustrates what his colleagues called "his uncanny foresight in anticipating chemical trends." Bleach was the company's big bread-and-

butter product. He tore down the bleach plant in 1915 and substituted for his chlorine cells new ones to recover caustic soda (sodium hydroxide) and chlorine with hydrogen as a by-product. With this drastic move he also forsook his pet idea of raw brine and in a series of triple-effect vacuum evaporators also recovered sodium chloride, magnesium chloride, and calcium chloride. The waste "mud," flushed periodically from the chlorine cells in the sewer, thus became three potential raw materials.

Carbon tetrachloride and chloroform introduced the company to organic synthesis, a field they cultivated with outstanding success. Both chemicals were first synthesized in the United States by Dow, and "carbon tet" was the first synthetic organic to reach big tonnage production.

Dow's great expansion during the World War I years was in several respects unique. Production of 30 million pounds of caustic, 23 million pounds of phenol, and over a million pounds of acetic anhydride were mighty contributions to the war effort, and the company filled big gaps in our chemical armory by supplying phenol and indigo, mustard gas (dichlorethyl sulfide) and metallic magnesium for flares, all new products of Dow research. Most of the wartime production was sold to the U. S. Government "at cost," and an audit of these thousands of accounts by the Cleveland Trust Company showed a net profit of 1-2/3 per cent. That also was Dr. Dow's way.

But conversion of this tremendous war effort to peaceful purposes was a typical Dow achievement. Taking phenol as an example—at the end of the war there was on hand a surplus of nearly 40 million pounds, seemingly a six-year peacetime supply. Dow had an unshipped stock of 4 million pounds and a new phenol plant almost ready to go into production. Unexpectedly the phenolic resin business boomed, and within three years three of the wartime producers were reactivating their plants. Not Dr. Dow—he wanted not the conventional sulfonation of benzol, but a new, more efficient process from chlorobenzene. Everyone said it could not be made to work, but Dr. William J. Hale perfected it, and in 1925 when Dow phenol came back on the market, the price dropped from \$.36 to \$.21.

Except for metallic magnesium during the closing years of his

life, Dr. Dow's chemical hobby was always bromine, and back in 1909 he had highly amused one of his chemical stockholders by forecasting a demand for his favorite of over a million pounds a year. He did not quite live to see his company producing a million pounds a month, but he did see test runs that assured him a process had been worked out to extract bromine from the sea which made such a fantastic output perfectly possible.

This undreamed demand was for ethylene dibromide, needed for the production of tetraethyl lead, the gasoline antiknock.

Outside of the company Herbert Dow had three absorbing interests. First, the city of Midland, which he found a wretched, unpaved, half-abandoned lumber town and left a model community. Second, his orchards and gardens where he turned 160 acres of sandy, cut-over land into a veritable Eden, a true show place, famous for its charm and beauty, an exceptional horticultural museum of rare fruits and flowers.

His third great interest was his family. From the days when as a bride Grace Ball helped him pick the specks out of bromide crystals to the years when he was head of one of the country's chemical enterprises, a bank director, a man of many philanthropies, Grace Ball was his helpmate, comrade, and confidant. In Midland, her memory is as warmly cherished to this day as his is. They had seven children and, save a boy who died young, all grew up and married: Willard, who succeeded him as president of the Dow firm, to Martha Pratt; Alden, the famous architect, to Vada Bennett; Helen, to William J. Hale; Ruth to Leland I. Doan, who in turn succeeded his brother-in-law to the company's presidency; Margaret to Harry Towsley; and Dorothy to Anderson Arbury, a physician and dentist, of Ann Arbor and Mirland, Michigan.

On October 15, 1930, Herbert Dow died at the Mayo Clinic, having failed to rally from a serious operation. He left the company he founded three valuable legacies: a tradition of bold, ceaseless research for new products and better processes; the habit of painstaking engineering, aimed always at the continuous operation automatically controlled; an example of corporate management distinguished for its friendly, human relations with its own people, its cordial cooperation with its neighbors, and its straightforward dealing with the rest of the business world.

NOTES AND REFERENCES

- The official biography, Murray Campbell and Harrison Hatton, "Herbert H. Dow: Pioneer in Creative Chemistry," New York, 1951, is excellent in its step-by-step development of Dow's chemical ideas.
- The chapter in Williams Haynes' "Chemical Pioneers," Van Nostrand, New York, 1939, pp. 259-78, is interesting for a personal interview setting forth Dow's chemical philosophy.
- Dow's Perkin Medal address and those of J. T. Pardee and E. O. Barstow, were printed in full in *Oil, Paint & Drug Repr.*, 21, Jan. 13, 1930; see also *Ind. & Eng. Chem.*, 22, 113 (1930); *Am. Dict. Biog.*, XXI, 261; "Who Was Who," I, 336.
- Obits: *Midland (Mich.) Republican*, Oct. 15, 1930; *Detroit Free Press*, Oct. 16, 1930; *Am. Dyestuff Repr.*, 671, Oct. 27, 1930.
- For Dow Chemical Company; H. H. Dow, *Dow Diamond*, February 1938, p. 69; Mark E. Putnam, "Twenty-five Years of Chemical Engineering Progress," *Am. Inst. Chem. Engrs.*, 1933; Williams Haynes, "American Chemical Industry," 6 vols., New York, Van Nostrand, 1945-54, VI, 113-24.

WILLIAMS HAYNES

.. 87 ..

Alfred Werner

1866-1919



ALFRED WERNER, son of a factory foreman, was born in Mülhausen, Alsace, on December 12, 1866. His predilection for chemistry became quite noticeable while he was still attending the lower schools, and when only about eighteen he submitted for criticism the results of his first independent chemical investigation to Emilio Noelting, who was then director of the school of chemistry at Mülhausen. In 1885, Werner entered the army and served a term as one-year volunteer at Karlsruhe and at the same time attended Engler's lectures on chemistry at the technical high school. The next year he moved to Zürich and in this city he made his home the rest of his life.

Three eminent chemists, Lunge, Hantzsch, and Treadwell were then teaching at the Eidgenössisches Polytechnikum (now called the Eidgenössische Technische Hochschule) and they were responsible for Werner's excellent training. After receiving his diploma as technical chemist, 1889, he became assistant to Lunge; and at the same time, as co-worker with Hantzsch, began the study of purely scientific problems. His doctorate thesis, "On the Spatial Arrangement of the Atoms in Nitrogen Compounds," was accepted by the University of Zürich in 1890. Werner then spent one semester in Paris studying with Berthelot at the Collège de France. On his return to Zürich, he applied for a license to teach at the Polytechnikum, submitting with his application a dissertation, "Contributions to the Theory of Affinity and Valence." In this he disposed of many traditional notions and laid the foundations of a new valence theory. In the autumn of 1892, when only twenty-six, he published "A Contribution to the Constitution of Inorganic Compounds," a paper which later became quite famous, for it marks its author as the founder of the modern views in this field and insures to him a rank in the history of chemical thought equal to that of August Kekulé.

Only one year later, in the fall of 1893, he was appointed successor of Viktor Merz, becoming extraordinary professor of chem-

istry and director of chemical laboratory A at the University of Zürich. Two years later he was promoted to a full professorship. He soon became one of the best known and most highly respected teachers and investigators at the University. Flattering offers from Vienna (1899), Basle (1902), the Eidg. Technische Hochschule (1905), and Würzburg (1910) were declined. Honorary doctorates were conferred on him by the University of Geneva and the Technical High School in Zürich. He was elected honorary or corresponding member of numerous scientific societies. Among the latter were the Königliche Gesellschaft der Wissenschaften in Göttingen; the physikalisch-medizinische Sozietät in Erlangen; the physikalischer Verein in Frankfurt; the Société de physique et d'histoire naturelle in Geneva; the Société impériale des amis d'histoire naturelle, d'anthropologie et d'ethnographie in Moscow; Chemical Society of London, etc. The Swiss Chemical Society honored him by establishing a Werner Fund and also issued a Werner plaque.

The highest scientific honor, the Nobel Prize, was awarded to him in 1913, and this occasioned a most enthusiastic ovation to their master by his students at Zürich. Even at this time, a serious disorder, arteriosclerosis, was beginning to make its destructive action evident, and at the end of 1915 he no longer felt able to deliver the general lectures. He resumed these at intervals but never for long, and finally the progress of the disease compelled him to relinquish his professorship in 1919. On November 15, 1919, death released this brilliant investigator, not yet fifty-three, from his distressing illness. He died while mentally deranged.

Werner was a plain, sincere character, possessed of a simple, candid disposition and endowed with high intelligence and firm determination. With a prodigious capacity for work and an endurance that seemed almost inexhaustible, he persisted at his theoretical and experimental problems, overcoming all human and material obstacles until he had reached his goal. It is obvious then that Werner was not an easy taskmaster to those working under his direction; his demands on them seemed often to reach the limits of possibility. However, this strict training certainly was a great asset to many of his pupils throughout their entire lives.

Especially in his younger years, Werner made it a practice to

discuss the newer work appearing in the literature or his own investigations for hours with his assistants and he demanded that sharp criticism be exercised during these sessions. His assistants did not always find it easy to follow the trend of his thoughts, for he had a fabulous memory which extended over the whole field of chemistry, both inorganic and organic, and he could pass from one subject to another with great facility. If the topic chanced to be, say, the isomerism of inorganic complex compounds, the discussion in a few moments would very likely be centered around analogous phenomena exhibited by terpenes, alkaloids, or dyestuffs. He insisted that his auditors have clear knowledge of the constitution and configuration of the individual compounds and be able to work freely with these concepts. He personally found no difficulty in these fields as he had a remarkable faculty for envisaging spatial relationships.

Under circumstances more favorable than those obtaining at Zürich, this eminent investigator would doubtless have established a large school of chemical thought. Nevertheless, his Zürich laboratory produced numerous men who occupy prominent places in the chemical industries and a goodly number of eminent teachers. Among these are Berl, Diltthey, Dubsky, Jantsch, Karrer, Pfeiffer, Schaarschmidt, and Stiasny.

He lectured only on organic chemistry until 1902 when he also took over the inorganic division. His lectures were well prepared, original in the arrangement of the material, and characterized by the clarity with which even the most complicated problems were treated. His delivery was convincing, and he exhibited such enthusiasm for his science that his hearers were carried with him.

His teaching abilities were also evidenced by his two principal books, of which the more important is "New Ideas in Inorganic Chemistry." In this he examined critically a vast mass of scattered data which were then, for the first time, classified systematically by means of his coordination theories. His "Stereochemistry" was also of fundamental importance, for it was the first comprehensive, critical treatment of this important field. Even present-day investigators of stereochemical problems find it necessary to refer repeatedly to Werner's text.

Werner developed a personal technique for his experimental

researches on organic complex compounds. On his laboratory table stood several microburners and microfilter supports, together with several hundreds of small glass dishes, whose contents were of all colors. Although none of these dishes was labeled, he was quite sure that confusion was almost an impossibility. The laboratory in which he did his first work consisted of very inadequate rooms, those in the basement well deserving their popular designation, "the catacombs." In 1909, he had the pleasure of moving into a spacious new laboratory built from his own plans. From this issued, in particular, his important researches on optically active inorganic compounds.

Werner's wife, née Emma Giesker, a native of Zürich, was a member of an immigrant German family. He also showed great affection for his children, one boy and one girl. He was a very sociable soul, finding recreation from mental toil among his friends in billiards, chess, or a Swiss card game, jass. A few weeks of the fall vacation were usually spent in the mountains; he did not enjoy longer pleasure trips. He was an ardent attendant of scientific conventions, and frequently lectured in foreign countries.

As a native of Alsace, Werner's cultural sympathies were both French and German, but he always emphasized that German science was responsible for his professional training. Of his teachers he especially revered Arthur Hantzsch. His published articles almost without exception appeared in German journals, and his books were also written in that language. However, his sympathies were with France during World War I.

Even the first of Werner's scientific papers, his doctorate thesis, written at the age of twenty-four, is of considerable importance since in it he laid the foundations of a new chapter of stereochemistry, namely, of nitrogen. Although published in the *Berichte* under the names of Hantzsch and Werner, the latter alone is responsible for the fundamental idea, viz., that in the numerous compounds of trivalent nitrogen (oximes, etc.), the three valence bonds of the nitrogen atom are directed toward three corners of a tetrahedron, whose fourth corner is occupied by the nitrogen atom itself. In this article, Werner successfully combated the views of V. Meyer and K. Auwers who sought to explain the isomerism of the benzil oximes by denying in this case the validity of the van't

Hoff principle of the free rotation of singly bound carbon atoms about the C—C axis. His excellent extension of the van't Hoff theory of the stereochemistry of carbon has been substantiated throughout. The experimental development of his new views is due especially to Hantzsch, as Werner's participation was not for long. Problems of an entirely different kind soon absorbed his interest.

Only a year after the appearance of his "Stereochemistry of Nitrogen," his habilitation essay, "Contribution to the Theory of Affinity and Valence," was published in 1891 in the *Vierteljahresschrift der Züricher Naturforschenden Gesellschaft*, and because of the limited circulation of this periodical the new ideas were only tardily recognized. This paper was a forerunner of Werner's masterly coordination theory. In this paper of 1891, he pursues a totally new path; he rejects the usual concept of valence as a directed single force; and assumes that affinity is an attractive force originating at the center of the atom and acting uniformly toward all parts of the surface. (For the sake of simplicity, the atom was imagined to be spherical.) Valency for him, then, became an empirical number concept. He succeeded in deriving the van't Hoff configuration formulas without assuming directed single forces; he worked out an acceptable interpretation of stereochemical arrangements, and attacked the benzene problem from a new angle. These ideas were developed at greater length in 1906 in a paper, "The Variable Affinity of Simple Compounds," and in conjunction with Thiele's theory of partial valence have been extremely fruitful for organic chemistry.

Werner's greatest achievement was without doubt the establishment of the coordination theory, with whose aid the young investigator, only twenty-six, cleared the way for a new phase of development of inorganic chemistry. According to his own statement, the inspiration came to him like a flash. One morning at two o'clock he awoke with a start; the long-sought solution of this problem had lodged in his brain. He arose from his bed and by five o'clock in the afternoon the essential points of the coordination theory were achieved. (In this connection, see the article on Werner in the *Schweizerische Chemikerzeitung* for 1920.)

The significance of Werner's coordination theory may be better

appreciated if it is pointed out that chemical compounds are conveniently classified as of the first order and as of higher orders (molecular compounds). As compounds of the first order are considered all those whose molecules are made up of two distinct atomic species (chlorides, oxides, sulfides, nitrides, hydrides, etc.). In this class are also placed those substances which are derived from these simplest compounds of the first order by replacement of single atoms by either atoms of another species or by groups of atoms (radicals). This includes the vast majority of the almost inconceivably large number of organic compounds. The Kekulé valence theory has proved absolutely essential in systematizing all these materials; its success is a veritable triumph.

Werner rejects the application of the Kekulé valence theory to molecular compounds, and to a certain extent he places them in a separate category, developing a new theoretical basis which permits of an orderly, comprehensive arrangement of even these compounds and, furthermore, his assumptions lead to a simple explanation of numerous cases of isomerism exhibited by these substances.

According to Werner's hypothesis, inorganic molecular compounds contain single atoms which function as central nuclei, around which are arranged in simple, spatial geometrical patterns a definite number of other atoms, radicals, or other molecules capable of independent existence. The figure expressing the number of atoms grouped around one central atom of a molecular compound was designated by Werner as the coordination number of this atom. The concept of coordination number, to which are also joined the concepts of "auxiliary valence number and force" and "indirect linking," forms the central point of the Wernerian system. Only a few coordination numbers come into consideration, the most important being 3, 4, 6, and 8. The number 6 occurs especially often. Thousands of molecular compounds of cobalt, chromium, platinum, etc., correspond to the 6 type. In all of these, as Werner pointed out in his first paper, the spatial configuration is octahedral in that around the central metal atom lie the six coordinated atoms in the corners of an octahedron.

This mode of representation was so novel and departed so

widely from all previous proposals that only a few of Werner's fellow chemists recognized the import of his ideas. The chief obstacle was the "organic" orientation of the majority of the chemists of that time, for that branch of the science was then experiencing great triumphs. Werner now entered upon a twenty-year period of experimental work, whose intensity has hardly ever been equaled. He and his co-workers constantly prepared new series of molecular compounds and studied their constitutions and configurations. More than 200 dissertations were produced under his direction; his own publications exceed 150. The structure of the chemistry of inorganic complexes revealed itself in more and more harmonious form and finally, after eighteen years, he made the important discovery of the optically active inorganic compounds, whose existence he had foreseen from his octahedral hypothesis. This constituted the experimental proof of one of the most important deductions of his theory, and in consequence the great significance of the coordination theory for the chemical systematics was generally recognized.

Now began the triumphant march of the coordination theory, but its author could no longer take an active part in its progress. Starting from a study of the metal-ammonia salts and of the double salts, two classes of materials which were then not considered of particular importance or interest, this theory, while still under Werner's guidance, embraced almost the whole of systematic, inorganic chemistry and its tentacles extended into the organic field, where today its importance is commonly acknowledged. Coordination concepts are playing an increasingly important role in crystallography, for it appears that, in general, crystals are built up in conformity with these teachings. If, in addition, it is assumed that these same considerations are valid in the theory of adsorption and of solution—although all this is still in the course of development—the comprehensive significance of Werner's life work follows as a matter of course.

Particular interest attaches to the question as to whether Werner's train of ideas was the culmination of a lengthy logical series of developments; i.e., whether it is possible to name certain individuals who had preceded him in more or less clearly recognized

essential portions of his theories. In the writer's opinion, this is not the case. Of course, in formulating his coordination theory, Werner employed certain ideas arising from Kekulé's valence theories, from van't Hoff's stereochemistry, and from the electrolytic dissociation theory of Arrhenius. The structure of his teachings appears, however, to have been erected as an entirely independent creation. This becomes especially evident if Werner is compared with Jörgensen, to whom (preceding and contemporaneous with Werner) is due credit for fundamental studies of the metal-ammonia salts, Jörgensen did not wish to break away from the usual inflexible valence theories; his formulas could not give lasting satisfaction, for they aroused no incentive to a further development of chemistry. Furthermore, Jörgensen was not sufficiently informed regarding the inner, theoretical, and experimental relationship of all the various classes of molecular compounds.

Mendeleev was perfectly aware of this inherent connection. In his text "Foundations of Chemistry," which Werner knew in its German translation, he clearly emphasized the constitutional similarity of metal-ammonia salts, hydrates, and double salts; indeed he also included alloys and solutions in his discussion. However, his attempts to bring order out of this chaos were not successful, although he did demonstrate that the pure valence formulations then in vogue could not be maintained. He was also correct in his systematic placement of certain series of compounds, such as polymeric metal halides, Al_2X_6 , etc. (which he considered as double halides). The privilege of reaching the goal toward which Mendeleev had turned his thoughts was reserved for Alfred Werner, whose creation of the general coordination theory was the work of a genius.

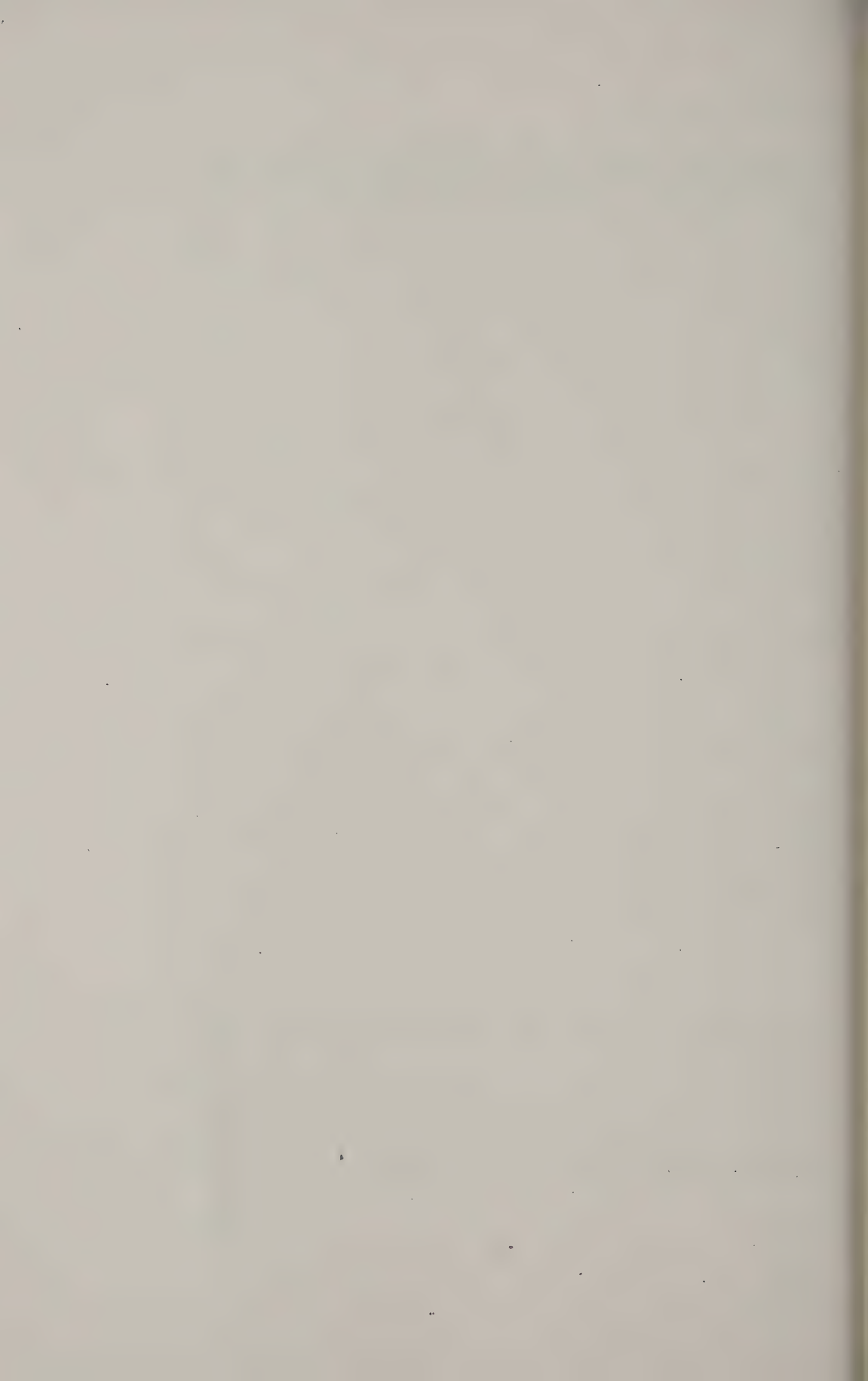
REFERENCES

- Karrer, P., *Helv. Chim. Acta*, 3, 196 (1920). Männer der Technik, 1925, p. 290, Herausgeber C. Matschoss; *Schweizer. Chemiker-Zeit.*, 1920, p. 73.
- Pfeiffer, P., *Z. angew. Chem.*, 33, 37 (1920).
- Lifschitz, J., *Z. Elektrochem.*, 26, 514 (1920).
- Morgan, G. T., *J. Chem. Soc. (London)*, 117, 1639 (1920).
- A practically complete bibliography of Werner's publications may be found in *Helv. Chim. Acta*, 3, 225 (1920).

ALFRED WERNER

From: *J. Chem. Educ.*, 5, No. 9, 1090 (1928). Translated by
Ralph E. Oesper. Original German article appeared in "Deutsches
Biographisches Jahrbuch, 1917-20," Stuttgart, 1928.

PAUL PFEIFFER



.. 88 ..

Wilder Dwight Bancroft

1867-1953



IN 1632, twelve years after the *Mayflower* sailed from Southampton and during the period of the "Great Migration," John Bancroft, accompanied by his wife and two young sons, left his English home in Norfolk to take a farm near Lynn, in the colony of Massachusetts. Although he died soon after, his son Thomas became the progenitor of a long line of stalwart churchmen and farmers; and, during more than a hundred and thirty years, five generations of Bancrofts developed a tradition and pattern of life which, as it has been said, "combined civic duties, rock-ribbed Calvinism and farming in equal proportions."

This seemingly settled and unchanging pattern and way of life, however, was shattered when, in November 1775, a son, Aaron, was born to Samuel Bancroft, farmer and deacon of the church in Reading, Massachusetts, and his wife Lydia Parker. Looked upon, even as a boy, as the "family rebel," Aaron liked neither the occupation nor the Calvinistic creed of his father, and, breaking with long-established tradition, he became a prominent Unitarian minister, a leader of the schismatics, and a soldier of the Revolution. He also wrote a "Life of George Washington," which enjoyed considerable popularity; and it was his constant prayer that he might be granted a "teachable temper."

The character and cultural mutation introduced by Aaron into the Bancroft line was continued and confirmed in his son George: scholar, politician, and diplomat; Secretary of the Navy under President Polk and founder of the U. S. Naval Academy at Annapolis; U. S. Minister in London and in Berlin; author of "History of the American Revolution" and of "History of the Formation of the Constitution of the United States of America." By his first wife, Sarah H. Dwight, he had two sons and a daughter; and the elder son, John Chandler, named after his grandmother, Lucretia Chandler, wife of Aaron Bancroft, became the father of Wilder. It is, I believe, in the mental qualities, outlook on life, personality, and character of his grandfather and great-grandfather, that we can

find the key to the personality and character of the subject of this notice.

Wilder Dwight Bancroft was born on October 1, 1867, at Middletown, Rhode Island, a small town and residential suburb of Newport, R. I. He was the elder of two children whom his father had by his first wife, Louisa Denny, daughter of a mill-owner, who died when Wilder was only four years old. Bancroft's father had studied law and was associated for a time with a firm of stock-brokers in Boston, but he later devoted himself to painting and studied art in France. His love of art, however, did not pass to his son. As a boy, Bancroft attended Roxbury Latin School and Milton Academy, where he showed outstanding ability, but little is known of his special interests or aptitudes during that period of his life. It was not, apparently, until he became an undergraduate at Harvard University in 1884 that any particular interest in science began to develop.

At that time, the senior professor of chemistry at Harvard was Josiah P. Cooke, whose books, "The New Chemistry" and "First Principles of Chemical Philosophy," may entitle him to be regarded as a pioneer of the older physical chemistry, and whose deductive method of approach to the study of chemistry cannot but have exercised an important influence on Bancroft's mind. There is little known about Bancroft's interests in science while at Harvard, but he showed prowess on the football field and was a member of the Harvard football team.

On graduating A.B. in 1888, Bancroft was appointed an assistant in the chemistry department. In the following year he proceeded to Europe where he worked more especially under Wilhelm Ostwald in Leipzig (1890-2), and under van't Hoff in Amsterdam (1892-3). He also spent some time at Strasbourg (1889-90) and in Berlin. In 1892 he presented a thesis entitled "Oxydationsketten" and after the usual oral examination was awarded the degree of Ph.D. by the University of Leipzig. In Amsterdam he continued his electrochemical studies and carried out experiments of an exploratory character on the chemical potential of metals.

On returning to America in 1893, Bancroft took up his former post as assistant at Harvard and in the following year was promoted to the rank of instructor. In 1895 Professor Cooke died and

Bancroft left Harvard to join the staff at Cornell University as assistant professor of physical chemistry. In 1903 he became professor and, in 1919, World War Memorial professor of physical chemistry. Thereafter the whole of his life was spent at Cornell. In 1937 he retired from his chair, and for a year was visiting Tallman Professor at Bowdoin College, Brunswick, Maine.

For more than forty years Bancroft was a member of the staff of Cornell. They were very strenuous years, but years which were full of work in which he could find satisfaction and happiness; and as time passed he became one of Cornell's best known and most outstanding professors. As a teacher he sought to impress on his students something of his own high character and enthusiasm for scientific truth. He lectured interestingly and clearly, using the original memoirs as the basis of discussion. His aim was not so much to impart a knowledge of a large number of facts as to impress on his students the importance of thinking things out for themselves; and he assessed the merits and standing of a student not by the range or number of facts which he was able to commit to memory, but by his willingness and ability to think and to draw his own conclusions from the facts discovered by himself or by others. To make people think may, perhaps, be regarded as a major aim of Bancroft's many writings, and the success with which he achieved this aim may be reckoned as among the most important of his contributions to the advancement of physical chemistry in America.

To younger chemists in whom he detected merit, Bancroft gave much help and encouragement, and there are not a few who have since attained to positions of eminence in chemistry, who look back with gratitude to the stimulus, encouragement, and help which they received from him.

Bancroft was interested in teaching, in making known to others what he had learned himself. He was obsessed with the importance of chemistry and he strove to make its importance more widely known and appreciated. "It should be the aim of all chemists," he wrote in the Jubilee volume of the *Journal of the American Chemical Society*, "to have chemistry take its place as the fundamental science," and he also urged physical chemists "to develop the borderlands between physical chemistry and the other sciences, such

as, biology, geology, physics, medicine, engineering, psychology, etc." Nor was it on his students and fellow scientists alone that he wished to press the importance of chemistry. Its importance must be recognized by the community as a whole, and he suggested that universities should teach chemistry as a cultural study—as part of a general education. He urged, also, the institution of courses of public popular lectures on chemistry for those not to be chemists—"chemistry of or pertaining to all the people"—pandemic chemistry, he called it. Bancroft drew up a syllabus of such a course, a course not to teach a man chemistry but to teach him about chemistry, but he recognized, as all teachers have recognized, that the success of such a course depends more on the teacher than on the syllabus.

In 1895, physical chemistry—the newer physical chemistry of which Arrhenius, van't Hoff, and Ostwald were the pioneers—was only in its infancy in America, and Bancroft, with boundless energy and full of missionary zeal, sought, on joining the staff at Cornell, to develop this branch of science. In his view, physical chemistry was not merely a branch of chemistry but covered the whole of chemistry, and he aimed at presenting the science as a complete and systematic whole.

While in Amsterdam, Bancroft had no doubt become acquainted with the work of Bakhius Roozeboom and had become impressed with the importance of the phase rule as a basis of classification of heterogeneous systems and as a guide in their investigation. Although it owed its discovery to the great Yale mathematician, Willard Gibbs, there was, in America, almost no knowledge of the great generalization or recognition of its practical importance. There was, moreover, no exposition in English by means of which the student could become acquainted with it. Bancroft, therefore, set himself the task of making good this deficiency and published his first book, "The Phase Rule," in 1897. In this work, at the cost of what must have been much labor, he collected together in a systematic manner the existing items of knowledge scattered throughout the literature, and was, as Bakhius Roozeboom wrote, "exceedingly successful in making clear the coherence of the phenomena and in presenting an inspiring picture of the imposing science of heterogeneous equilibria." Unfortunately he was not

quite successful, as he himself admitted, in producing a book which a student could read with profit and without difficulty. Nevertheless, it was a remarkable work to be written by one who was under thirty years of age and still on the very threshold of his teaching career. Along with the many papers written by Bancroft and the experimental work carried out by his pupils under his inspiration and guidance, "The Phase Rule" constituted a very important pioneering advance into a domain which, later, was vigorously and fruitfully cultivated in America. As Bancroft pointed out, the renowned Geophysical Laboratory at Washington is a wonderful example of what can be done with the phase rule as an instrument of research.

It is, perhaps, worthy of note that Bancroft, in this book, introduced into phase rule terminology the words nonvariant, monovariant, divariant, etc., suggested to him by his colleague, Joseph E. Trevor.

In his desire to further the study of physical chemistry in America, Bancroft no doubt recognized, as Ostwald in Germany had recognized, that if this new branch of science was to grow and develop, it must have a special organ through which it could express itself, and so, in 1896, he founded *The Journal of Physical Chemistry* as "an organ for the publication of research in all branches of experimental and theoretical physical chemistry." Until 1932, Bancroft was editor of the *Journal* (associated during the first thirteen years with J. E. Trevor), contributed many articles to its pages, and wrote also for it many book reviews and abstracts of scientific papers published elsewhere. Not only did Bancroft found the *Journal of Physical Chemistry* and thereby, it may be, rendered his greatest service to chemistry, but he also financed it out of his private resources. In 1924, when the financial burden became too great for him, he handed the *Journal* over to the American Chemical Society, the Chemical Society, and the Faraday Society, under whose auspices it was published until 1932. In 1947 its title was altered to *Journal of Physical and Colloid Chemistry*. It would be impossible with any accuracy to assess, as it would be difficult to exaggerate, the value and importance of this journal in promoting the development of physical chemistry in America by uniting the workers in this new domain of knowledge,

by giving them their own organ of publication and thereby making effective advance possible.

From 1913 until his death, Bancroft was also associate editor of the *Journal of the Franklin Institute*, an institute founded, in 1826, in the State of Pennsylvania, to "diffuse information on every subject connected with the useful arts." To this journal Bancroft contributed, in 1925, an article on the development of colloid chemistry.

The numerous papers on emulsions, colloids, adsorption, etc., which from just before the First World War appeared in the *Journal of Physical Chemistry* under the name of Bancroft and of his pupils, were evidence that a new interest, one which became, perhaps, his strongest and most enduring interest, had developed in Bancroft's mind.

For some time interest in the colloid state had been growing in America, as in Europe, and although books on colloid chemistry existed, they had been written, in Bancroft's opinion, in too purely descriptive a manner and presented the subject empirically. By 1920, he considered that theory had developed sufficiently to allow the data to be presented deductively, and this he sought to do in his "Applied Colloid Chemistry," which first appeared in 1921 and of which two further editions were published, in 1926 and 1932.

This book, in its enthusiastic presentation of the subject, its critical sifting of reputed facts and explanations which the author regarded as doubtful or conflicting, its stimulating suggestiveness of how information gained in one field of investigation may be applied in many other fields, is entirely characteristic of Bancroft and deals clearly and comprehensively with a wide range of facts and observations. It is a book which is not only interesting and easy to read, but is sometimes almost entertaining, as when Bancroft writes: "There is one experiment which I always like to try, because it proves something whichever way it goes. A solution of iodine in water is shaken with bone-black, filtered, and tested with starch paste. If the colourless solution does not turn starch blue, the experiment shows how completely charcoal extracts iodine from aqueous solution. If the starch turns blue, the experiment shows that the solution, though apparently colourless, still contains iodine which can be detected by means of the sensitive starch test." One

can almost see the engaging twinkle in his eyes as he carries out this experiment in front of his class.

Although Bancroft was the author of only two books, writing, with him, may almost be said to have been an inherited characteristic, and he wielded the pen with ease and dexterity. He was an omnivorous reader and a voluminous writer, living constantly under the urge not only to seek out truth but to proclaim to others the truth when found. He had a wonderfully retentive memory and was a great encyclopedist. In the many papers which he published in the *Journal of Physical Chemistry* and elsewhere, and in the numerous lectures and addresses which he delivered, Bancroft sought to bring together the facts already known, to sift them carefully and critically, to point out what he regarded as errors or defects in the interpretation of experimental data, to indicate what, in his opinion, were the fundamental problems to be investigated, and to put forward generalizations for testing by experiment. Ideas, suggestions of problems for investigation, sprang in almost bewildering profusion out of an extensive knowledge and exuberant imagination; and not a few of these problems were thereafter investigated by Bancroft's pupils in his laboratory at Cornell and under his stimulus and direction. It is, I believe, in his numerous writings and in the stimulus and encouragement which he gave to workers in widely different fields to take the data and conceptions from one branch of study and to consider their application to another, that we find Bancroft's chief contribution to the advance of scientific thought and knowledge.

Tall and strongly built, robust both physically and mentally, and with a fair and fresh complexion, Bancroft looked out on a world which was to him so full of interest, through blue eyes from which a smile was never far distant. Throughout most of his life he retained as a spectator an enthusiastic interest in athletics, especially baseball and football, in which, in his younger days, he had gained no little distinction. Independent, as always, of the opinions of others, Bancroft was also inclined to be unconventional in dress. Van't Hoff tells how, during a visit which he paid to Bancroft in 1901, he was surprised to see his host dressed in knickerbockers and shoes, and how he reminded him somewhat of an *impressario*. He recounts, also, a somewhat hair-raising ex-

cursion to Taughannock Waterfall which he and his wife made in a horse carriage with Bancroft as driver. By some mistake they had got on to a road long disused and they had to descend and push or pull the carriage over the roughest parts, or even to lift it over a water conduit. However, they all arrived back again without serious mishap, and van't Hoff committed his feeling of relief to his diary in the words, "How fortunate we were to have such a safe driver as Wilder."

Bancroft found relaxation mainly in playing golf, and he was one of the organizers of the Country Club at Ithaca. He greatly enjoyed taking part in national and international congresses and conferences where he could discuss scientific problems with fellow workers. On such occasions, his genial and enthusiastic manner and his witty talk ensured for him a cordial welcome.

Bancroft was ambidextrous and, when lecturing, he liked sometimes to astonish and impress his audience by a demonstration of his ambidexterity. Standing at the middle of the blackboard he would begin to write a line with his left hand and then, transferring the chalk but without altering his position, would complete the line with his right hand.

On June 19, 1895, Bancroft married Kate Bott, of Albany, N. Y., whose father had emigrated from Germany to the United States about the middle of the nineteenth century, and whom he had first met during his period of study in Berlin in 1893. She died in February, 1942.

In 1937, when Bancroft retired from the active work of his chair, he was still in the enjoyment of good health and could look forward to spending the evening of a very busy life in the unhurried, happy, and peaceful pursuit of his scientific interests. But this was not to be. In 1938, after returning from Bowdoin College, he was run over by a motor car on the Cornell Campus and received very severe injuries. For several months he lay in the hospital and, although, thereafter, he was able to move about quietly with the help of a walking stick and to pay occasional visits to the chemistry department, he never fully recovered his health. A year or two before he died he fell out of bed during another period in the hospital and was then confined to his home.

During his many years of partial or complete invalidism Ban-

croft, undaunted by the cruel rub of fortune, remained cheerful and retained his interest in science and athletics; and smiling into the frowning face of Fate, he fulfilled his allotted span of life. Peacefully, on the morning of February 7, 1953, he died in his sleep.

Bancroft is survived by two sons and three daughters, of whom the eldest is married to M. L. Nichols, professor of chemistry, Cornell University.

With his alert and wide-ranging mind, with his independence of outlook and fearlessness in expressing his views, which were in no way inferior to those of his New England forebears, Bancroft was an outstanding personality and exercised a great influence on the development of physical chemistry in America. It may be that in his editorial chair Bancroft was apt to regard himself not only as the professor but also as the autocrat of physical chemistry; it may also be that with his unusually wide knowledge and confidence—not unjustified—in his own judgment, he was inclined to be intolerant of the views of others when they differed from his own and to express his criticisms not only freely but, occasionally, with an unnecessary acerbity of language, and so was apt to make personal enemies of those who, through association in work and community of interests, should have been his friends. If, in the interests of scientific truth, he provoked controversy; if sometimes he even seemed, almost wilfully, to revert to the character of his grandfather, "the aggressive partisan who appeared to court unpopularity," yet in the social relations of everyday life how considerate and lovable he could be, how gracious and charming his manner, how interesting and entertaining his conversation. He died leaving a wealth of achievement as his monument and a treasured memory that will not quickly fade.

Bancroft's scientific interests were very varied and evidence of his encyclopedic mind is given in the numerous papers and articles which he wrote on electrochemistry, oxidation-reduction cells, and overvoltage; phase rule; osmotic pressure and dilution law; contact catalysis; corrosion; colloids and emulsions; hydrogenation; charcoal; theory of photography and the photographic plate; photochemistry; structural colors; proteins; coloring of glass by metal oxides, etc. To discuss here his scientific contributions in detail

would be impossible; and one must restrict oneself to indicating only some of the more important aspects of his scientific work.

In the Preface to his "Phase Rule," Bancroft classified the facts and phenomena of physical chemistry into the divisions: Qualitative Equilibrium, Quantitative Equilibrium, Electrochemistry, Mathematical Theory. "My idea," he wrote, "is that all qualitative experimental data should be presented as particular applications of the Phase Rule and the Theorem of Le Chatelier, while the guiding principles for the classification of quantitative phenomena should be the Mass Law and the Theorem of van't Hoff." The view thus expressed explains no doubt why, when Bancroft first began his studies of heterogeneous equilibria with the investigation of ternary mixtures, he approached the subject not from the standpoint of the phase rule but from that of the law of mass action.

At a time when the systematic study of heterogeneous equilibria was still in its early years, Bancroft and his pupils made many valuable contributions to the advancement of knowledge in this domain, a general discussion and exposition of the principles of the phase rule marching hand in hand with the experimental investigation of a wide variety of systems. It is possible to deal here only with some of the most important aspects of Bancroft's work in this field.

Organic chemists had made known the existence of isomeric substances which could exist in two different solid forms, each corresponding to a single definite constitution, but which, in the liquid state, could undergo transformation one into the other until a state of homogeneous equilibrium between the two molecular species was established. The behavior of such substances gave rise to much controversy, and Bancroft was the first to show that many of the observed facts became more intelligible when one studied the heterogeneous solid-liquid equilibria met with in the case of these "dynamic isomerides." To the value of his work in this domain Ernst Cohen paid tribute in the words: "Einen nicht unwesentlichen Dienst bei dieser Zeit- und Streitfrage auf dem Felde der 'geometrischen' Isomerie haben auch physikalisch-chemische Untersuchungen geleistet, so namentlich . . . das Studium der Gleichgewichtsverhältnisse von Bancroft."

The behavior met with in the case of dynamic isomerides de-

depends on the rate of transformation of the one isomer into the other in the liquid state. If the transformation is relatively very rapid, so that equilibrium in the liquid state is rapidly attained, the system will behave like a one-component system; but if the isomeric change is comparatively slow, the behavior will be that of a two-component system; and, in the absence of compound formation between the isomers, a two-branched freezing-point curve will be obtained.

If isomeric transformation takes place with measurable velocity and if the temperature of the liquid equilibrium mixture is allowed to fall, a point on the freezing-point curve of one of the solid isomers will be reached, and that form will separate out, if supercooling is excluded. This is called the "natural" freezing point. The stable solid modification in the neighborhood of the melting point is that which is in equilibrium with the liquid phase at the natural freezing point.

The two solid modifications of dynamic isomerides may be monotropic or enantiotropic. It was found by Soch, working in Bancroft's laboratory, that in the neighborhood of the melting point, the yellow form of benzil-2-carboxylic acid, melting at 141.5° , is the stable form, whereas, at room temperature, the white modification, melting between 125 and 130° , is the stable form. Investigation showed that there is a transition point at about 65° . The two isomeric forms are therefore enantiotropic.

The behavior of a number of different dynamic isomerides was investigated by Bancroft's pupils.

The boiling-point curves of binary liquid mixtures were also investigated by Bancroft and his pupils. Among the mixtures which show a minimum in the boiling-point curve it was found that in many cases one or both of the components is associated. The reason why in such cases a minimum is obtained was first explained by Bancroft as due to the fact that the boiling-point curves of such components intersect.

In other directions, in the investigation of the freezing-point equilibria in three-component systems, in the indirect determination of the composition of the solid phase separating from two-component systems, etc., Bancroft and his pupils were pioneers. At a much later period, when Bancroft's interests had extended to

biochemical phenomena, use was made of phase-rule principles in the investigation of the behavior of proteins toward hydrogen chloride and ammonia. It was shown that casein, zein, arachin, fibrin, and gliadin form no chemical compound with ammonia, and that casein, arachin, fibrin, gliadin, and edestin, but not zein, form definite compounds with hydrogen chloride.

To Bancroft's interest in colloids and the colloid state reference has already been made. In his mind, colloid chemistry, which he defined as "the chemistry of life and inheritance and of bubbles, drops, grains, filaments and films," extended over almost the whole field of chemistry and physical chemistry.

Of the subjects which at an early stage attracted Bancroft's interest, one may mention the preparation and properties of emulsions.

In order that a permanent emulsion may be produced on shaking together two immiscible liquids, e.g., water and oil, an emulsifying agent, such as soap, must be added. It is, of course, clear that two different emulsions are possible, an emulsion of oil in water and an emulsion of water in oil. According to the adsorption-film theory of emulsions put forward by Bancroft, an emulsifying agent is adsorbed into the surface separating the two liquids and forms there a coherent film. This film, if in contact with two phases, oil and water, will have two surface tensions, and will tend to curve toward the side having the higher surface tension. The dispersed liquid, therefore, is on the side of the film having the higher surface tension. Since soaps of univalent cations (Na^+ , K^+) are readily dispersed in water but not in oil, they form a film which is wetted more readily by water than by oil. Consequently, the surface tension is lower on the water side than on the oil side, and the film tends to curve so that it encloses globules of oil in water. Thereby the area of the side of the film of higher surface tension is reduced compared with that of lower surface tension. Soaps of bivalent cations, however, are freely dispersed in oil, but not in water, and the film is wetted more easily by the oil than by the water. Thereby the formation of globules of water in oil is favored. According to this theory, the preferential wetting of the adsorbed film by water or by oil is an important factor.

The theory put forward by Bancroft was investigated more fully

by his pupils, more especially by G. H. Clowes, and the antagonistic action of Na^+ and Ca^{++} on oil-water emulsions established. This antagonistic action of ions has been found to be of great importance not only in the interpretation of many biological phenomena but also in the oil industry.

In Bancroft's view, surface adsorption was a factor of the greatest importance in many diverse phenomena. In the development of the photographic plate, for example, Bancroft was the first to suggest that adsorption of the developer on the silver bromide grain is the important thing, a view which was later worked out more fully by Sheppard. "If the reducing agent is adsorbed much more strongly by exposed silver bromide than by unexposed silver bromide, the former will develop more rapidly than the latter, and we shall get a negative. If the reducing agent is adsorbed more strongly to unexposed than to exposed silver bromide, we shall get a positive. If there is not much difference in the adsorptions, we shall have exposed and unexposed silver bromide developing at so nearly the same rate that we get a more or less uniform fogging."

Sensitizers, also, of the photographic plate, Bancroft pointed out, must be such that the dye is adsorbed strongly by the silver bromide, does not bleed into the gelatin sufficiently to act as a color screen, and is a reducing agent powerful enough, when exposed to light, to produce a latent image on silver bromide.

In 1922 the First Report, and in the following year the Second Report, of the National Research Council's Committee on Contact Catalysis were published in America. Both reports were written by Bancroft, the chairman of the committee, and were a very stimulating and valuable contribution to the study of contact catalysis. In these reports, which appeared at a time when contact catalysis was largely an empirical art, Bancroft not only showed the position which had been reached but also pointed out what were the fundamental questions which had to be answered and indicated many problems, minor or major, which called for investigation.

For Bancroft, contact catalysis formed an aspect of colloid chemistry and embraced phenomena in which adsorption and surface action play an important part. Two things of fundamental importance, he suggested, had to be done: (1) to determine in what

cases definite intermediate compounds are formed, and what they are; (2) to determine what bonds and contravalencies are opened when adsorption takes place and to show that the opening of these bonds and contravalencies accounts for the formation of the reaction products. Later, Bancroft pointed out that the attempt to determine in which group a particular reaction falls, whether there is formation of definite compounds or of indefinite complexes, had led to the brilliant work at Princeton on catalysis at an interface.

In the activation process, however, adsorption is only one factor. "In organic chemistry we get activation and reaction as a result of the formation of radicals . . . The conclusion to be drawn is that the organic chemistry of the future will deal with the reactions of radicals instead of the reactions of the molecules."

Even if it might be difficult to point to direct experimental contributions by Bancroft to the solution of the problems of contact catalysis, there can be no doubt that through his writings he did much to define and clarify the *science* of catalysis and to encourage others to carry out the necessary experimental investigations.

Towards the end of his academic career Bancroft took up the study of anesthesia, drug addiction, and insanity from the standpoint of colloid chemistry. It can be accepted that for the normal, healthy functioning of the animal organism, a certain balance must be maintained between the degree of dispersion or the hydration and dehydration of the body colloids. Starting with Claude Bernard's theory that the reversible coagulation of the colloids of the sensory nerves produces or accompanies anesthesia, Bancroft and his co-workers concluded from their experimental investigations that narcotics coagulate reversibly the cell colloids and, conversely, that a reversible coagulation of the cell colloids, however produced, will cause narcosis. At low concentrations, narcotics may have a stimulating effect by decreasing the stability of the colloids. Similarly, the action of drugs, such as morphine, is due to a coagulation, reversible or irreversible, of the nerve colloids. Administration of peptizing agents, such as sodium thiocyanate, will facilitate return to normality.

A relation between the state of flocculation or deflocculation of the brain colloids and mental disorders was also believed to have

been established, different forms of mental disorder depending on whether the coagulation of the colloids was too great or too little.

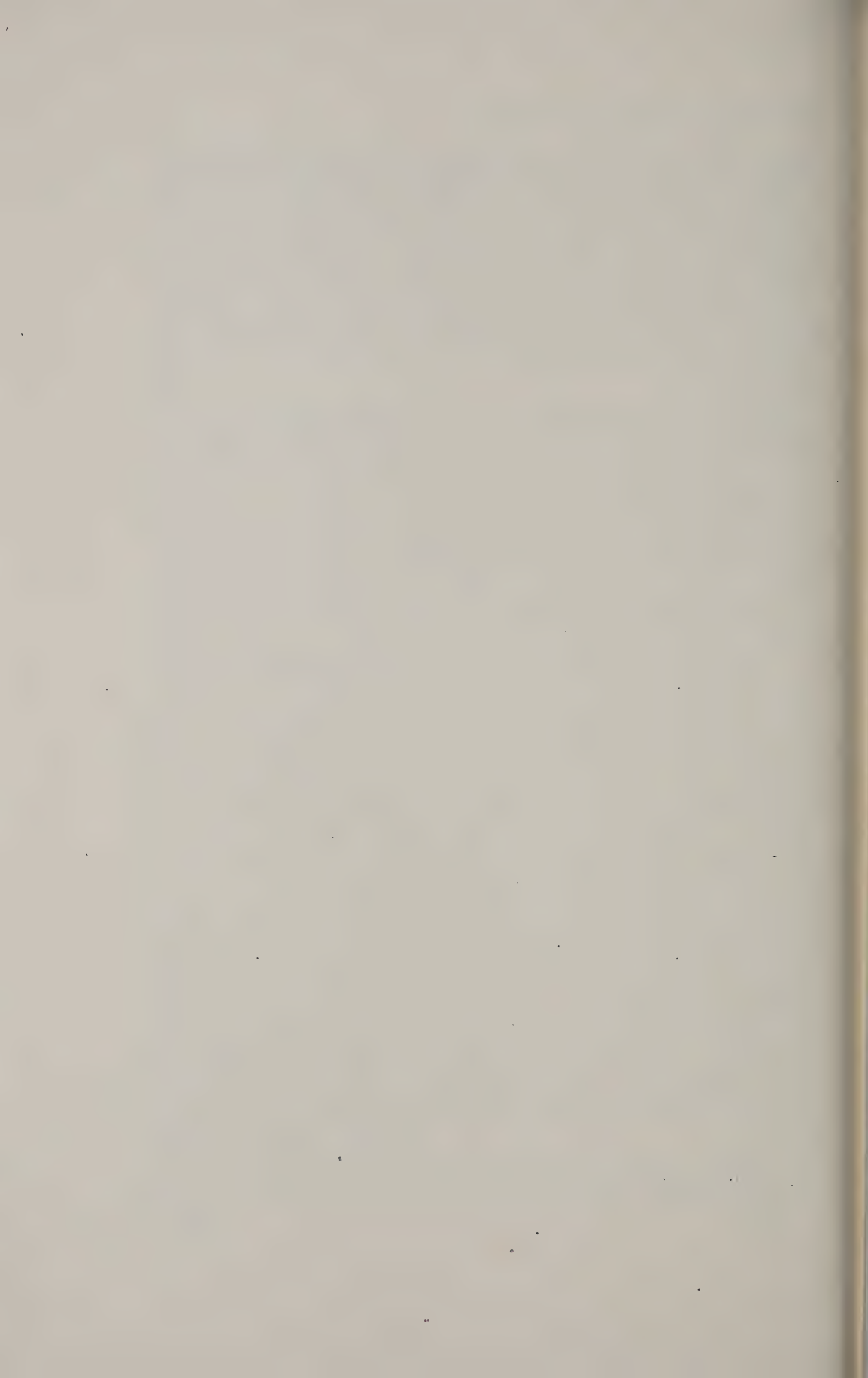
The conclusions reached by Bancroft and his fellow workers led to much controversy and were not entirely confirmed by other research workers. It seems very clear that, although the state of aggregation or dispersion of brain colloids no doubt has a bearing on the physiology of narcosis and insanity, factors of importance other than those considered by Bancroft enter in and affect the colloid state.

On many other problems in colloid chemistry and other sections of physical chemistry, Bancroft shed a powerful light which was both exploratory and clarifying, and the inspiration of his enthusiasm and critical exposition still lives.

For particulars about Bancroft I am indebted more especially to his son-in-law, Professor M. L. Nichols, of Cornell University.

From: *J. Chem. Soc. (London)*, 1953, pp. 2506-14, abbreviated.

ALEXANDER FINDLAY



.. 89 ..

Marie Curie

1867-1934



A STROLLER in the Latin Quarter of Paris in the winter of 1897 who happened to look into a small building used for storage on the rue Lhomond—that part of old-Paris where the French preserve by the street names the glory of their scientists—would have seen a tall handsome man with a brown beard and a woman with a beautiful intellectual face gazing intently at some glass receptacles which were aglow in the darkness with a curious greenish light; even a thin vapor arising from some of the fluid in the basins was faintly luminescent. This couple was Pierre and Marie Curie, who after a day of hard labor in their workshop returned after dinner, as they frequently did, to see that things were all right for the night and to wonder at this curious auroral glow that was produced by the hitherto unknown element, radium, which they were in the process of isolating from the ores of uranium. This faint luminescence was due to the alpha rays which the radium and its emanation gave off, bombarding the atoms of the air, changing their chemical nature and exciting their electrons, and the Curies were observing the birth of the world of the infinitely little and the dawn of the new alchemy. Though they did not know it, their discoveries were to revolutionize the opinions of 2000 years, completely transform modern physics, aid astronomers in their study of the stars, restore to life and health thousands of human beings, and inspire a host of investigators along innumerable lines of study in wholly new fields. It is of interest to discuss briefly what led to this remarkable discovery, for in science no one stands alone; if Röntgen had not discovered in 1895 the rays which bear his name, the name of the thirty-year-old Marie Curie might never have been known to fame.

About the year 1890 physics was supposed to be more or less finished, for it was felt that all the important laws had been discovered, and the only thing remaining was to measure the known phenomena more accurately. It is true that certain scientists in England and Germany were studying the luminous bands and other phenomena which occur when a fairly high-voltage elec-

trical current is passed through a glass tube containing various gases at low concentration. Faraday and Crookes were two who had spent time on this subject without casting much light on its nature. About 1890 an English physicist, J. J. Thompson, studying the effects of the transmission of electricity through rarefied gases, began to make observations which pointed to the fact that the explanation of the luminous phenomenon must be that under the influence of electricity the gas in these laboratory aurora is broken down into electrified particles, for the colored streamers were deflected by a magnet or an electric current outside the gas-containing tube, as Plücker had described in 1858.

It was while working with such a tube in 1895 that Roentgen noticed that photographic plates lying on a table nearby were fogged, and in a few months the discovery of x-rays was made. He, as Plücker in 1858 had noted, saw that the glass of the tube assumed a bright greenish color while the current was passing, and it was thought at first that this greenish color was the source of the radiations.

Poincaré, the famous French mathematician, showed the first x-ray pictures taken by Roentgen at a meeting of the Paris Academy of Sciences in January, 1896, and in the discussion which followed made this same suggestion as a possible explanation in reply to a question by Henri Becquerel. The father of Becquerel had been a famous chemist, and the son possessed a considerable supply of uranium salts which had come into his possession after his father's death.

Uranium salts give off a greenish phosphorescence when exposed to light, so Becquerel covered some photographic plates with black paper, laid the uranium salts on them together with some metal objects and, to his astonishment, found that he had a Roentgen shadow picture. Being a scientist, he tried some uranium which had not been exposed to light and found that it photographed just as well. Then he took some fresh samples of very pure, recently prepared uranium and found that it did not photograph. Becquerel recognized that the photographic effect must lie either in the atoms of the uranium or in a contaminating substance present. Today we know that the uranium breaks down in the course of years into radioactive substances. For a long time these rays were called

Becquerel rays. Becquerel was unable to continue these investigations and suggested, late in 1897, to Pierre and Marie Curie, who shortly before had been married, that they follow up this discovery and find out what was the substance in uranium which possessed photographic capacities.

This selection had a touch of genius in it, for Pierre and Marie Curie combined that persistent and clear-sighted intellectual energy which is so necessary for scientific discovery. They were poor, struggling to do work under disadvantageous conditions, and gladly turned to this new field where Pierre Curie's knowledge of physics and Marie Curie's knowledge of chemistry were needed to solve the problem. In 1898 they announced the discovery of radium.

There has been much discussion as to the part which each played in this discovery. Marie Curie has always said that it was a combination of two closely related minds. It was her duty to do the arduous chemical analyses which were necessary to find the minute traces of radium in the ores with which they worked. They tested all the minerals in the college collection and found a few which had photographic power and also were capable of ionizing the air about them so that it would carry a minute electric current instead of acting as a very perfect insulator, as does ordinary air. These ores were chiefly those containing uranium. It was Pierre Curie's share, as a trained physicist, to take each substance—and there were over thirty known elements in the uranium ores—and determine, with an apparatus which he had invented some time before, the amount of ionization that each sample produced. Thus, as they eliminated metal after metal, they finally found that mixed with bismuth and barium were minute traces of intensely ionizing substances. The first was polonium, the second radium.

The quantity of current which flows when the ionization is produced is a measure of the radioactivity of the element. Radium salts are never sold by weight, but by the ionization which they produce as compared to a standard, and the x-ray used in the treatment of cancer is also measured by this means. In this phase of their work they fell back upon the discoveries which had been made in the past showing that not only x-rays made air a conducting medium, but that all gases became conducting when a

current of electricity was passed through a glass tube containing a rarefied gas, thus returning to the early work of Faraday and others who had noted this phenomenon.

Now we know that the currents through these tubes or through what is called an ionization chamber are produced by the separation from a gas of the electrons, a swarm of negatively charged particles so minute that we shall never be able to see them, which themselves being charged with electricity or, according to the modern view, consisting of an electrical charge, are able to transfer a current by moving from one pole to another. Faraday many years before had brought forward a similar idea to explain the conduction of electricity through fluids and the basis of all electrical deposition of metals which had long before reached a practical development, as every piece of Sheffield plate testifies, for the silver in a solution of silver salt is carried from one pole and deposited upon the copper, which forms another pole. Today we know that x-rays are produced by the beating of these electrons upon the surface of a metal, which so perturbs the atoms of that metal that they radiate x-rays, just as an electric current in the ordinary lamp bulb heats the filament and makes it give off electrons, as Thomas Edison showed in 1883 without knowing the explanation.

Thus Marie Curie by her chemical discovery of the element radium inaugurated what may be called modern physics, and it must have been to her a marvelous satisfaction that her daughter, Irène Joliot-Curie, has followed in her footsteps, making one discovery after another, which would render the name Curie imperishable had her mother never been famous. But it has been granted to no other woman so to revolutionize by a single discovery the whole subject of atomic physics.

When Pierre Curie in 1903 found that radium gave off heat, many of the theories of physics, especially that dealing with the conservation of energy, seemed to be shattered, but shortly afterward it was shown that this heat was produced by the breaking down of the atoms of radium, and the heat production could be accounted for by the slow, spontaneous destruction of this newly discovered element which in some 1700 years loses half of its substance. The final stage which this breakdown reaches is lead, a

lead which cannot be distinguished from the ordinary plumber's lead except by the most refined methods of analysis.

In passing, it may be said that this fact has been used to measure the age of the earth, for the minerals which contain uranium also contain lead and the amount of this lead gives a measure of the number of years that the uranium has been in existence. Hence, like the rings of the great redwood trees in California which show that they are the oldest living creatures, so the amount of radium lead in minerals points to millions of years of life of an ore in which the original uranium has been slowly changed through a series of breakdowns into lead.

The first radium obtained was very impure, and after 1898 Pierre Curie interested himself in the physical properties of this new substance and discovered that it gave off particles which could pass through air for a distance of one to two inches and then suddenly stop. These are now known as the alpha particles from radium and are actually electrified atoms of helium gas. The gamma and beta rays, the latter being negatively charged particles, were found by others, chiefly Rutherford.

Marie Curie then devoted herself to the separation of large quantities of radium from the residue of many tons of uranium ore from Joachimstal in Bohemia, which were placed at her disposal by the Austrian government. After years of hard work requiring a most laborious series of chemical separations and crystallizations of the impure product, she finally succeeded in making a small quantity of absolutely pure radium, the chemical properties of which she studied. She also prepared sealed tubes containing carefully measured amounts of the pure salts which are deposited in the various bureaus throughout the world, including the Bureau of Standards in Washington, to serve as standards for the measurement of radium, just as the standard meter and standard yard are deposited and used for the checking of accurate measuring instruments.

In the meantime, a host of investigators, including the famous Lord Rutherford, who died only a few months ago, began to investigate this profitable field. The Curies had noticed in 1899 that all the apparatus and even the walls of the room in which they worked became radioactive. It was soon found that radium gave off

a gas which is now known as emanation or as radon. This gas is really the active substance which characterizes radium, for, if the gas is pumped off, radium ceases to radiate, but in the course of a few days regenerates more radon, which can again be pumped off and used for practical purposes, for a great deal of the treatment of cancer is done with radon rather than with radium. This radon gas has a very short life, losing half of its value in a little over three days.

Further studies showed in the course of the breakdown of radium that a large number of products were obtained, some with an extremely short life measured in thousandths of a second, others which lasted for millions of years. In the uranium-radium family there are sixteen known members, the last being lead. It was soon found that thorium also possessed radioactivity, and the thorium family has thirteen known members, ending again with lead. Later a actinium family was found, also of many members, and its termination is also in lead. But this was the work of other hands.

Others also invented elaborate theories for the constitution of matter based upon Marie Curie's discoveries. We believe for the moment that an atom of matter is composed of a central nucleus, which contains neutrons and fragments of hydrogen known as protons, and around this as a center rotate the electrons, one for hydrogen and up to 92 for uranium, the metal with the highest atomic weight. The Curies vaguely dreamed of this celestial system with a central sun and surrounding planets, and Irène Curie just missed the discovery of the neutron by a few months. The central mass of neutrons and protons determines the nature of the element and the electrons control its chemical reactions. The electrons can be pulled off by exposure to Roentgen or gamma rays and heat. This does not change the actual chemical nature of the substance, for the atom which has been stripped of some of its electrons collects these quickly from neighboring atoms and becomes normal again. In a gas this recovery takes only a few minutes. But Lord Rutherford showed, in 1919, that if alpha particles from radium are allowed to play upon nitrogen gas some of the nitrogen is destroyed and changed into oxygen and hydrogen. Apparently the helium particle is able to break into the center of the atom and change the atomic weight, for nitrogen has an atomic

weight of 14 and the oxygen produced of 17. Helium with an atomic weight of 4 and nitrogen with 14 make an atomic weight of 18 against the oxygen with 17, leaving a missing weight supplied by hydrogen with an atomic number of 1. Both helium and hydrogen can be found in the sealed tube originally containing only nitrogen. This was the first artificial production of new elements and is the field in which Irène Curie has made herself famous.

Whether the radium which Marie Curie discovered will ever be produced artificially by some such process is as yet unknown. Probably it will be found that the amount of energy used up is so enormous that the transformation must remain a laboratory experiment, but Professor Ernest O. Lawrence, of California, has produced several pounds of radioactive sodium by bombarding ordinary salt with atomic bullets, which has certain interesting uses in that if a small quantity is placed on a person's tongue and an electrical machine attached to his foot, it will be found that this sodium is in a few moments in the general circulation, thus testing the speed of absorption. Radioactive iron is being used to study the way in which anemia is cured by iron, and a host of interesting problems have developed from this work. All these things are mentioned merely to show the marvelously fertilizing effect of a single important discovery.

In the light of all these astonishing events it seems as if the pioneer work of Marie Curie was very simple, but this is because the facts have become a part of everyday knowledge and it is the gift of the genius such as this woman possessed to interpret the results of simple chemical analyses, and to infuse into dull decimals a life of the spirit. Thousands of chemists could have done the analytical work which she did, as she employed merely textbook methods, but in her mind lay the power to conceive theories to explain not only what had already been discovered but to open paths for further investigation. In many instances she was unable to carry these on in person, but they were immediately seized upon by others who used the ideas which she had developed to make important discoveries.

Her mind was an extraordinary one. She had no interest in people in general or for the ordinary matters that fill the minds of

so large a proportion of the world. She cared nothing for names and titles, as some amusing incidents related in a recently published biography by her daughter, Eve Curie, show. She cared only for a few friends and her scientific work. In this field she had the power of enormous and prolonged concentration on a problem. In her later years, despite serious ill health, she worked in a variety of fields and contributed to all of them. She studied the causes underlying the destruction of cells by radium, for example. During World War I, when her laboratory was closed, she applied herself to the practical use of x-rays and did valuable work in organizing and directing a field system of portable x-ray machines by which surgeons could be guided in the treatment of injured soldiers. It must have greatly pained her, who longed to benefit the human race by her labors and refused to patent or accept money for her method of refining radium, to know that the discovery of radium, which has meant so much for the saving of human life, was also used extensively to coat luminous tapes to guide soldiers through the barbed wire entanglements of the battlefields and to illuminate gunsights in order that men might shoot each other with greater facility.

Her direct contributions to the treatment of cancer were few. She was immensely interested in the work of the Curie Institute under Dr. Claude Regaud, for which she was responsible, and was of great help in teaching the staff the technique of preparing and measuring the radium they were using.

It was interesting to see her mind at work. As she passed through the great Physical Laboratories of Columbia University on her first voyage to America she must have thought of the abandoned storehouse in which she had worked. While nothing interested her but some of the subjects with which she was familiar, she would immediately stop and discuss any work in her own field with a member of the staff, wholly forgetful of time, appointments and the friends who wondered why she did not turn up for lunch, concentrated and interested in the new things that she was able to see in other people's investigative labors. There was not one atom of jealousy in her nature.

That she was a genius there can be no doubt. True, all genius is aided by circumstances and she might have remained a teacher of

chemistry in a French school if it had not been that Becquerel made and tested an erroneous theory, and as a result an opportunity was given to her to investigate a new field of science. But it is true also that many others were working in the same direction, but had failed to accomplish anything.

The argument has been made that because simultaneous discoveries are not infrequent in science genius is merely a question of mass action and if only a sufficient number of persons work on a problem, the discovery will be achieved. But since the pioneer work of Plücker in 1858 innumerable persons had run an electric current through an evacuated glass tube and studied the phenomenon which ensued, although it was not until 1895 that Roentgen found that every such tube gave off x-rays. It is related that one English scientist of great ability noted that his photographic plates were fogged in the neighborhood of such a tube, but instead of searching for the reason, he complained to the maker of the plates that they were defective and obtained a new box. Roentgen had the flash, the intuition, if you will, which made him find out why his photographic plates were fogged. So Marie Curie had the intuition which led her to devise the hypothesis that it was the breaking-down of the atoms of uranium which caused it to give off radiation. Without this working hypothesis radium might not have been discovered for another hundred years.

After her husband's death in 1906 Marie Curie was appointed to his chair of radio-physics in the Sorbonne and continued his lectures. In 1910 she published an important work, a "Treatise on Radioactivity" which summarized their labors and those of others up to that time. Later she wrote a charming memoir of her husband, which is too little known, although an admirable translation has been printed in this country. She also published a book on "Radiology and the War" which was drawn from her experiences in organizing a field radiological service for the French army. She continued her scientific researches despite continued ill health and published many short papers on various topics. Her laboratory became a center for research students from all parts of the world.

Much has been made, and I think too much, of the difficult circumstances under which the Curies worked, their poverty and the lack of appreciation in France in the early period of their dis-

coveries, but truly they lived an ideal life. They believed, in spite of her dreams for the emancipation of her native Poland and their desire to help humanity, that they were powerless to change the social order; that if they had had the power they would not have known what to do, and so in working without understanding they would never be sure that they were not doing more harm than good by retarding some inevitable natural evolution. In science, on the contrary, they felt they could accomplish more with their lives than in any other direction; that the field here was more solid and obvious, and however small a territory it might be it was truly their own possession. Marie Curie writes of her early days in Paris: "This life, painful from certain points of view, had for all that a real charm for me. It gave me a precious sense of liberty and independence. If sometimes I felt lonesome, lost in the great city of Paris, my usual state of mind was one of calm and great moral satisfaction. All that I saw and learned delighted me. It was like a new world opening to me, the world of science which I was at last permitted to know in all liberty." Of the abandoned shed which was the best laboratory the School of Physics could give them she writes:

Despite the exhausting work it was in this miserable old shed that we passed the best and happiest years of our life, devoting our entire days to our work. I shall never be able to express the joy of the untroubled quietness of the atmosphere of research and the excitement of actual progress with the confident hope of still better results. The feeling of discouragement that I sometimes felt after some unsuccessful toil did not last long and gave way to renewed activity. We had happy moments devoted to a quiet discussion of our work while walking around our shed.

Another and far different person has described the same sensation:

I do not know how far it is possible to convey to anyone who has not experienced it the peculiar interest, the peculiar satisfaction, that lies in a sustained research. It is a different thing from any other sort of human effort. You are free from the exasperating conflict with your fellow creatures that, for me, is its peculiar merit.

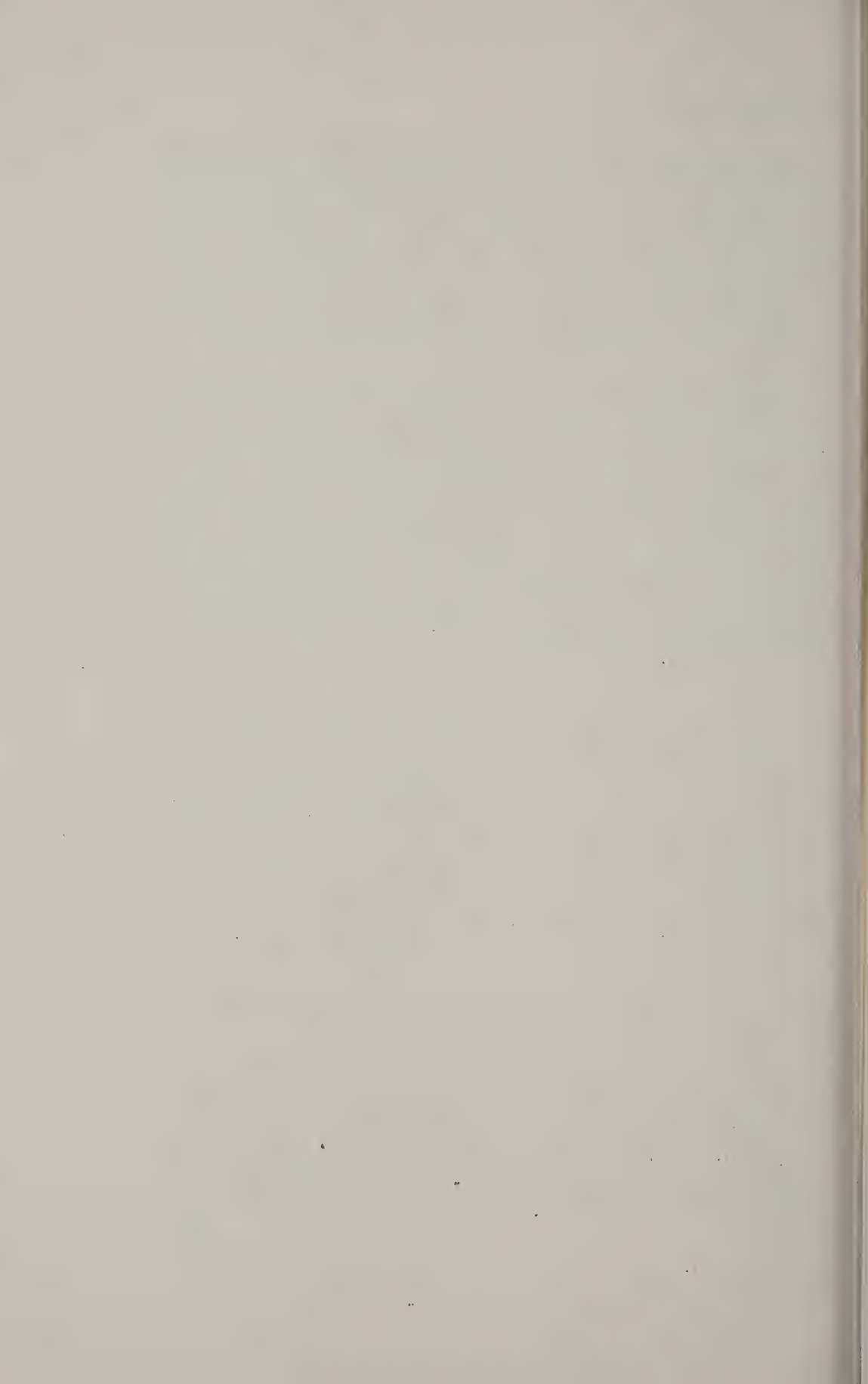
MARIE CURIE

Scientific truth is the remotest of mistresses. She hides in strange places; she is attained by tortuous and laborious routes. She is always there, winning you to her, and she will not fail you. She is yours and mankind's forever. She is reality. You cannot change her by advertisement or clamor nor stifle her in vulgarities. Things grow under your hands when you serve her, things that are permanent as nothing else is permanent in the whole life of man. That, I think, is the peculiar satisfaction of science and its enduring reward.

So I think that if Marie Curie had been asked in her last days, as she looked across to the sunlit mountains of Savoy from her room at the sanatorium at Sancellemoz, what her life had been, she would have replied that it had been full of human affection and companionship with one whom she loved, full of the joys of research, of hard work and of final achievement, crowned at last with the highest of human rewards, the admiration by the few great minds capable of understanding the superb nature of those discoveries which were hers and render her name imperishable as long as the human race exists.

From: *Sci. Monthly*, April 1938, p. 378, read at a memorial meeting held at Columbia University, New York, on Jan. 20, 1938.

FRANCIS CARTER WOOD



.. 90 ..

Vladimir N. Ipatieff

1867-1952



RUSSIA has produced many notable chemists, but three tower above all others. They are Lomonosov, Mendeleev, and Ipatieff. Of these it has been suggested that Ipatieff stands out as having "exerted greater influence on world chemistry than his two fellow countrymen."¹

An examination of Ipatieff's life and achievements shows three significant periods. The first period embraces his childhood, education, and progress up to and including his administrative work during World War I. The second period covers his work during the Russian Revolution, when he was active until 1930 in developing the Russian chemical industry as well as his scientific investigations. The third period includes the time from 1931 until his death on November 29, 1952, in Chicago, at the age of eighty-five.

Special emphasis will be given here to the first period, since in it will be found the clues to the development of his outstanding work and personality. The successes which he accomplished in his later life may be traced directly to his chemical experiences in this first period.

FIRST PERIOD, FROM 1867 TO 1917

Vladimir Nikolaevich Ipatieff² was born in Moscow on November 21, 1867 (according to the Roman calendar). His early education in reading and writing was provided by his mother, who was well educated and whose family was well represented in the intellectual aristocracy of occupations, such as teachers, tutors, mathematicians, and physicians.

Since his studies with his mother progressed slowly, however, he was entered in a local school where he remained for a couple of terms after which, at the age of eight, he was admitted to a preparatory class of the Fifth Classical Moscow Gymnasium.

His mother's impaired health and her removal to the Crimea resulted in his eventual withdrawal from the Classical Gymnasium to study at his father's home in Moscow, in order to prepare for admission to the second class of the Third Moscow Military Gym-

nasium. Following the usual custom among the Russian nobility, Ipatieff began to prepare for a military career. The loss of his mother's influence, at the age of ten, undoubtedly affected him in many ways. His mother died when he was twelve years old, and his governess, who later became his stepmother, was almost the antithesis of his mother: she was noted for her penuriousness, she generated neither love nor respect, and had no interest whatsoever in his or his brother's education. She also influenced the acquisition of certain religious prejudices, in spite of which he became a devout member of the Russian Orthodox Church.

An uncle who served as a private tutor to wealthy Moscow families provided him and his brother with additional education, and interested Vladimir in various extracurricular (scientific) subjects which were not part of the work of the gymnasium.

Upon promotion to the sixth class Ipatieff became interested in mathematics and studied it beyond class requirements. Although his teacher in mathematics considered that he had sufficient ability to study higher mathematics and that he should be admitted to an artillery or engineering school, his grades were too low and he was denied admission to the Mikhail Artillery Academy. Upon graduation he entered the Alexander Military School in Moscow on August 31, 1884.

Ipatieff's first serious interest in chemistry had started in the fifth or sixth class of the Third Military Gymnasium. When he entered the Alexander Military School his interest in science was renewed. In spite of unsuitable texts, ineffective teaching, and poor organization of laboratory work, chemistry interested him more and more, and as a result of his interest he finished at the top of his class with the highest grades in both mathematics and chemistry.

His real teachers were Mendeleev's "The Fundamentals of Chemistry" (third edition, 1884) and Menshutkin's "Analytical Chemistry." He read these books, carrying out the reactions and experimenting as he proceeded.

Ipatieff was made an officer on August 7, 1887. On becoming an officer each appointee received a sum of money from the government. Since this would not pay for everything, his father gave him some extra cash for clothing. Undecided for a time whether to buy a winter coat or a small chemistry laboratory, Ipatieff did not hesi-

tate long and, as might be expected, the laboratory was his choice.

In August, 1889, Ipatieff took a competitive entrance examination and was accepted by the Mikhail Artillery Academy, where his dream of devoting himself to the subject of chemistry was about to be realized.

Soon after joining the Mikhail Academy, Ipatieff learned of the Russian Physical-Chemical Society which was sponsored by St. Petersburg University. In spite of the fact that only graduates of institutions of higher learning were eligible, Ipatieff was admitted to membership in 1890 and remained a member until 1937, when the Soviet Government cancelled his membership and forbade Russian chemists to mention his name in their scientific publications. It was in the Society that he reported many of his scientific discoveries and came in personal contact with such scientific stars as Dmitri Ivanovich Mendeleev, 1834–1907, Nikolai Aleksandrovich Menshutkin, 1842–1907, Fedor Fedorovich Beilstein, 1838–1906, and others who were a great inspiration to him.

In 1891, in spite of his heavy work load at the Academy, he finished some analytical work on crystallization in steel. His paper was suggested and approved as a report before the Imperial Technological Society. Although he was not a member of this technical society, his paper, "Chemical Investigations of the Structure of Steel," was published in the Society's *Annals* in 1892. To his delight, he was asked to read his paper before the Russian Physical-Chemical Society at a meeting in March, 1892. The report was well received, and even the outspoken and critical Mendeleev, who was chairman, said a few words of approval.

Ipatieff's two chemical manuals published for Academy students, his work on the structure of steel, and his success in the field of chemistry and chemical technology marked him for appointment at the Academy as an instructor.

Soon after he received the appointment as instructor at the Mikhail Artillery Academy he married Barbara Ermakova, whom he had known for ten years.

At the Academy he lectured on theoretical chemistry and published a set of notes entitled "Principal Laws of Chemistry," which went into a number of editions. Besides all this, Ipatieff was required by Academy regulation to present an approved dissertation

to the Academy conference three years after his appointment as an instructor. Since Ipatieff was familiar with the literature of carbides (compounds of metals with carbon) he decided to present a dissertation on their preparation and chemical properties.

Toward the end of 1894 Ipatieff reported his discovery of dimethyltrimethylene glycol to the Chemical Society. As a reward for this discovery the Chemical Society gave him the Butlerov prize for the best work done by a young chemist.

Early in 1895, Ipatieff presented his dissertation. The final subject was "The Action of Bromine upon Tertiary Alcohols and of Hydrogen Bromide upon Acetylene and Allene Hydrocarbons in Acetic Acid Solutions."

The results obtained from Ipatieff's investigations reported in his dissertation had suggested to him that the same reaction should be studied with other types of hydrocarbons. At that time, diolefins containing two nonadjacent double bonds had been studied very little. The hydrocarbon C_5H_8 , isoprene, had long (1860) been known as a decomposition product of natural rubber and turpentine; but its structure was entirely unknown, and Beilstein's *Handbook* of 1895 placed a question mark after its formula.

Ipatieff immediately started to prepare isoprene by the dry distillation of raw paracaoutchouc. His study of isoprene was postponed, however, and it was not until 1897 that he proved its structure and then synthesized it.

During 1896 he was advised by A. E. Favorsky to continue his study of organic chemistry in Munich under the great Adolf von Baeyer. Baeyer's laboratory was equipped for some eighteen students who were working toward the Doctor's degree, and also a small number of postdoctorate research chemists, among whom were Willstätter, Beshorn, Gomberg, Piccard, and others. Ipatieff worked directly under Baeyer's supervision.

Ipatieff's nearest co-workers were Gomberg, the American, and Koch, the Englishman. Gomberg was born in the southern part of Russia, had emigrated to the United States at the age of nineteen and, fortunately for Ipatieff, could speak Russian.

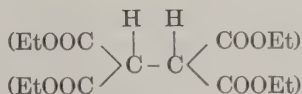
Ipatieff's work progressed rapidly. He obtained caronic acid and proved its structure. Considerable brown tar was formed during the reaction by the oxidation of carone ($C_{10}H_{16}O$, a cyclic ketone

of the terpene series) and when Ipatieff asked Baeyer what to do with it he always said, "Throw it out." Ipatieff thought he might extract some substance from this tar which would explain the low yield of acid. Keeping his work to himself, he managed to extract a new acid which turned out to be a spatial isomer of the first acid.

Back at the Academy Ipatieff's work in the laboratory was concentrated upon an investigation of the little-known allene class of hydrocarbons. The action of sodium malonic ester on the dibromides obtained from allene hydrocarbons and also the action of nitrosyl chloride upon the double bond were especially interesting to him. These investigations served later as the subject of his professorial dissertation.

Studying the action of sodium malonic ester on the dibromides of olefins (the Perkin reaction), he found that one does not always obtain a cyclic acid when one atom of bromine is located on the tertiary carbon atom in the dibromide, as was proposed by Perkin.

On the night of November 12, 1897, when his youngest son, Vladimir, was born, he went to bed on the couch in his study much later than usual. As he lay there he was haunted by this mysterious compound. Suddenly the idea came to him that it had the structure of acetylene tetracarboxyester



formed by the condensation of two molecules of sodium malonic ester with the loss of two atoms of sodium under the influence of the unstable dibromide. He jumped out of bed and looked in Beilstein's *Handbook* and was amazed and delighted to find that the physical and chemical properties given in the literature for this compound agreed perfectly with those of the compound that he had obtained.

Ipatieff had started to write his dissertation for the rank of professor in the fall of 1898, and by the end of that year it was ready for publication under the title, "Allene Hydrocarbons, the Reaction of Nitrosyl Chloride and of Nitric Oxide on Organic Compounds Containing a Double Bond, and the Synthesis of Isoprene."

In 1900 Ipatieff also became interested in unsaturated hydrocarbons, which induced him to study Thiele's method for the preparation of 1,3-butadiene by pyrolysis of isoamyl alcohol. Ipatieff found the yield of butadiene quite small. Little or no attention had been paid to the nature of the liquid products obtained in this reaction. Ipatieff investigated the residual liquid which he found to be isovaleric aldehyde when he used an iron tube in his experiments, but very little, if any, of this substance was formed when he used a glass tube. This work proved that pyrolytic decomposition which previously had been considered uncontrollable with the formation of products such as carbon, hydrogen, methane, ethane, ethylene, etc., could be controlled by the use of catalysts to produce individual compounds. Ipatieff was the first to recognize this important principle. As a further example, when alcohol is heated in the presence of brass, zinc, or copper, it produces acetaldehyde plus hydrogen, and when heated in the presence of alumina the products are ethylene and water. With these discoveries, the basis of Ipatieff's scientific career began to emerge.

From the very beginning of the study of the decomposition of alcohols in the presence of iron Ipatieff had realized that he was dealing with a new phenomenon which the Russian chemists called a contact reaction and other European chemists called a catalytic reaction. The novelty in his discovery was that these reactions could take place at high temperatures; previously it had been assumed that there was a complete breakdown of the alcohol molecule under such conditions, and that no clean-cut reactions would occur.

The discovery of the catalytic decomposition of alcohol into aldehyde and hydrogen opened an entirely new field of investigation for him. The reaction was one of catalytic dehydrogenation (the removal of hydrogen), and a detailed study was necessary to elucidate the mechanism and gather sufficient information to predict new catalysts for the reaction.

After reporting his first work in catalysis at the January, 1901, meeting of the Russian Physical-Chemical Society, he sent the article on the catalytic removal of hydrogen from an organic molecule to Berlin to be published in the *Berichte* of the German Chem-

ical Society. It was published in March of that year, which meant that his work appeared ahead of the first and famous article by Sabatier (Paul, 1854–1941) and Senderens (Jean Baptiste, 1856–1937) in the *Comptes rendus* on the hydrogenation of benzene in the presence of reduced nickel.

At another meeting of the Russian Physical-Chemical Society, Ipatieff gave a detailed report on the catalytic decomposition of alcohols under the influence of various metallic catalysts, and proposed a reaction mechanism. To test his hypothesis, he studied the catalytic effect of various metal oxides, and his views—that if a metal causes the aldehyde decomposition of alcohols its oxide should do the same—were completely confirmed.

In the fall of 1901 Ipatieff discovered the effect of alumina on olefinic decomposition of alcohol into ethylene. The enormous field of the dehydration of organic compounds opened before Ipatieff. He began by examining the catalytic action of silica, alumina, and finally clay, in the preparation of olefin from alcohol. Alumina proved to be the best catalyst.

In the spring of 1902 Ipatieff systematized his lectures in organic chemistry at the Artillery Academy and the following year used them as the basis for a textbook "Inorganic Chemistry" suitable for technical institutions and universities. In all, seven editions of this book appeared, and the later editions were considered especially useful for their systematic and understandable presentation of the different types of organic compounds.

Ipatieff's greatest discovery in this period (1903) was the isomerization of the olefin isopropylethylene into trimethylene and, also, that ether hydrocarbons, cyclic and open chain, could be isomerized in the presence of catalysts. These catalytic isomerizations attracted the attention of the scientific world, but they were not applied practically until thirty-five years later. It was not until the 1930's that the reactions were seriously considered by scientists as well as petroleum technologists as a means of obtaining high quality gasoline.

In 1903, Ipatieff showed for the first time that in the presence of powdered aluminum, ethyl alcohol decomposed at 600°C. to give not only aldehyde and ethylene but also butadiene. Later Lebedev

studied this reaction in greater detail and, by using mixed catalysts, so increased the yield of butadiene that this method could be used in the manufacture of synthetic rubber.

In 1903, also, in order to study the reversibility of reactions discovered in 1900, Ipatieff experimented laboriously for a whole year to construct an apparatus suitable for high-pressure work.

In the fall of 1904, using high-pressure technique, he began the study for hydrogenating organic compounds in the liquid phase. This study established for the first time the reversibility of catalytic reactions in the presence of such catalysts as nickel, iron and zinc.

In spite of the war between Russia and Japan, which began early in 1904, and the political disorders of 1905, Ipatieff was able to continue his research without interruption. The results obtained in this work as well as previous work started Ipatieff on the study of what was later called destructive hydrogenation. These data were used later by Friedrich Bergius (1884–1948), in decomposing various types of coals, tars, etc., in the presence of hydrogen to produce low-boiling hydrocarbons for motor fuels.

Toward the end of 1909 Ipatieff discovered a very interesting phenomenon while studying the hydrogenation of organic compounds containing a double bond. The hydrogenation of amylene or cyclohexene in the presence of a copper oxide catalyst is slow and incomplete in a bronze-lined, high-pressure bomb. But the reaction is rapid and complete in an iron bomb in the presence of copper oxide. The idea then came to him that the iron walls of the bomb increased the catalytic action of copper oxide. Ipatieff considered this one of the most important of his discoveries.

In 1911 Ipatieff showed for the first time the cyclization of aliphatic hydrocarbons. The formation of the abnormal product of polymerization—paraffin hydrocarbons—was explained as well as possible on the basis of the experimental data; a complete picture of its formation had to await further study. Not until twenty years later, when Ipatieff was in the United States, was he able (with his co-worker Dr. Pines) to study this reaction thoroughly in the presence of phosphoric acid catalysts. They were able to give a complete explanation of the formation of aromatic hydrocarbons. The formation of the latter from cyclized olefins must be

accompanied by the liberation of hydrogen, and it is this hydrogen that adds to the olefinic polymers to convert them to paraffins.

This complicated reaction of ethylene, which Ipatieff named "conjunct polymerization," is an example of intermolecular hydrogenation, hydrogen being removed from one molecule and transferred to another.

During 1912 Ipatieff hydrogenated carbohydrates at relatively low temperatures. Emil Fischer had reduced monosaccharides (glucose, fructose, and others) to the corresponding alcohols (mannite, sorbite, etc.) by means of sodium amalgam. Ipatieff's experiments indicated that hydrogen under pressure easily converts mono- and polysaccharides to the corresponding alcohols.

In 1912 Ipatieff showed for the first time that the reduction of carbon monoxide and carbon dioxide by means of hydrogen at a high temperature does not proceed to completion and that the reaction is reversible, that is, the water that is formed during this reaction can oxidize methane back again to hydrogen and carbon monoxide. This reaction was later used industrially for the production of hydrogen.

The desirability of studying the pyrolysis (cracking) of petroleum and its distillates under pressure, in the presence and absence of catalysts, for the purpose of obtaining gasoline was discussed with the director of Nobel Brothers Laboratory at Baku, Russia. (The Nobel Brothers Laboratory had been formed by Robert (1829–1896) and Ludwig (1831–1888), brothers of Alfred Nobel, founder of the Nobel Prize.) The director approved this idea, and permission was obtained from the Board of Directors to do work on it. When the first data were reported to the Board of Directors they decided to continue the investigations. The World War of 1914–1918 forced them to halt their work, and it was not published until 1920. When Ipatieff arrived in the United States in 1931 he became acquainted with the various American methods for cracking petroleum, and he realized that the processes were practically the same as those which he and his co-worker had worked out.

Investigations in 1913 dealt with both organic and inorganic compounds. He was particularly interested in the separation of

acids under pressure by means of carbonic acid. Experiments showed that carbonic acid can replace acetic acid from its salts, and when the carbonates of the metal are insoluble in water, the salt separates in the form of crystals.

That same year, a Finnish chemist, working under Ipatieff's supervision, made two investigations in the field of high pressure. His study of the polymerization of ethylene in the presence of catalysts was the more interesting. For the first time it was shown that ethylene polymerizes in the presence of aluminum chloride to a liquid at room temperature. This important discovery was later used by the petroleum industry for the production of gasoline from olefins and for the manufacture of synthetic lubricating oils.

Ipatieff's other consulting work was in the new branch of industrial chemistry—the hardening of vegetable oils into solid fats. As an industrial consultant Ipatieff spent part of his time studying various technical problems. Ipatieff carried out one series of experiments on different catalysts which might be suitable for the hardening of fats. The number of articles which were beginning to appear in English and German scientific literature on the application of metal oxides as catalysts in the hydrogenation of organic compounds indicated the influence of Ipatieff's work abroad.

From 1913 on, Ipatieff became more and more interested in the actual application of his scientific knowledge to the needs of industry. Unfortunately, the Russian chemical industry was too immature to use these scientific discoveries even then available. Ipatieff did not take out patents, indicating that he was a scientist and wanted complete freedom in his work, which he would not have if he had to be concerned with patents.

Ipatieff's research early in 1914 centered around the precipitation of zinc from a solution of its salt by means of hydrogen under pressure. According to the Nernst theory on the dissolving of metals, hundreds of thousands of atmospheres of hydrogen would be required to separate zinc from a solution of its salt. Ipatieff achieved this result at a pressure of 400 atmospheres and at 350°C.

In the Russian Empire before World War I, there was no department, despite the existence of the special Ministry of Trade and Industry, which could direct the development of Russia's national economy in time of war. The Ministry had little knowl-

edge of Russian industry as a whole, and it knew even less about its infant chemical industry. The history of the Russian chemical industry during the war and immediately after is best given by an account of the activity of the Chemical Committee of which Ipatieff was chairman. This committee united all branches of the chemical industry, it served the needs of the Army, and also prepared for the eventual return of industry to a peacetime role.

World War I brought new and responsible assignments to Ipatieff. The first of these was the organization of all chemical defense. Russia did not have a sufficient accumulation of munitions or individual munitions plants. In a short time Ipatieff mobilized all Russian industry for this work, and the production of explosives increased in six months from 60 tons per month to 3300 tons. In two years' time an enormous chemical industry was brought into existence, and Ipatieff was justly recognized as its creator. This and other items of interest are detailed in the Second Period.

SECOND PERIOD, FROM 1917 TO 1931

The second period of Ipatieff's life began with very trying days in Petrograd (now Leningrad). In this period a number of events in the life of Ipatieff are enumerated which proved trying, time-consuming, and ineffective. The accumulation of events forced upon Ipatieff the belief that scientific thought and expression would be continually curtailed and that freedom for such activities would, of necessity, need to be pursued elsewhere.

According to Ipatieff, the October Revolution (1917), masterfully led by Lenin, saved the country from anarchy, and at least temporarily preserved its intelligentsia and material wealth. Ipatieff also maintained that but for the Bolsheviks in 1917 and 1918 he probably would have lost his life.

Since the problem of changing the chemical industry from a wartime to a peacetime basis was paramount, Ipatieff, as chairman of the Chemical Committee, called a special meeting in January, 1918. The results were frustrating and indefinite, and little or nothing came from the discussion.

Life in Petrograd during 1919 to 1920 became more and more

unpleasant, and Ipatieff's research almost stopped. Toward the end of 1919 he acted as consultant in the reorganization of a soap and candle factory in Kazan. Later, he was sent to inspect government arsenals.

In 1920 Ipatieff became director of the National Institute of Scientific and Technical Investigations (formerly the Central Chemical Laboratory). Because of the acute sugar shortage in 1920, Ipatieff served as consultant to a small factory producing saccharin.

On the other hand, 1921 was a record year for Ipatieff. In order to speed the rebuilding of Russian industry it was voted to combine trade and industry under one commissariat as in the tsarist days. Ipatieff was asked to head the newly established Chemical Administration which was finally approved by Lenin and the All-Russian Central Executive Committee, with the assignment to secure foreign aid in the redevelopment program of the chemical industry.

In 1923, Ipatieff studied the destructive hydrogenation of naphthalene. It was demonstrated for the first time that molecules of polycyclic organic compounds can be cracked into simpler molecules without the formation of polymers or noticeable quantities of carbon. Also, naphthalene and tetrahydronaphthalene (the product of the hydrogenation of naphthalene) give a large quantity of aromatic compounds, such as benzene, toluene, etc., in the presence of the mixed hydrogenating catalyst nickel oxide and alumina.

Government duties occupied Ipatieff's time in 1923; that fall, in accordance with previous commitments, he spent a month in Germany negotiating for the production of mustard gas. This was followed in 1924 by work on the Russian-German Commission for the construction of poison gas factories. Research duties occupied the remainder of his time. During 1926 changes took place which strongly influenced Ipatieff's entire future in the U.S.S.R.

The Russian-German Commission on poison gas production had become very time-consuming, and the Chemical Administration meetings spent endless hours discussing current and tentative problems of the chemical industry. Ipatieff advised that Russia establish its own production of calcium cyanamide since this could

be used directly as a fertilizer for agriculture. This advice received slight consideration.

Also, there were many disputes over the future development of various branches of the chemical industry, particularly those relating to dyes and to nitrogen fixation. One of the most heated controversies had to do with the establishment of the production of naphthol by-products. Other unpleasant incidents occurred in carrying out Ipatieff's duties, and in the end Ipatieff decided to leave the Chemical Administration.

About this time also, significant changes in the independence of the Academy of Sciences were taking place. Within a year the government appointed a commission of academicians and party officials to discuss basic reforms which would ensure that the Academy's activities conformed in great measure to the needs of the Socialist government. This action ended the Academy's independence.

Toward the close of 1926 Ipatieff prepared to organize another laboratory for catalytic experiments under high pressure, the one at the Artillery Academy being too small for his needs. Accordingly, the year 1927 saw the official launching of the Institute of High Pressures in Leningrad, its expenses being included in the budget of the Institute of Applied Chemistry.

From the High Pressures laboratory Ipatieff and associates published more than twenty completed research reports during 1927 to 1928.

About this time Ipatieff was chosen as chairman of a commission to study the conversion of benzene and toluene to explosives. During the Scientific Week in Berlin to honor Russian scientists, Ipatieff, at a dinner given by Walther Nernst, met Albert Einstein. During the dinner Ipatieff was asked why he did not take up permanent residence abroad. He replied that he had not the slightest intention of leaving his country because he sincerely believed that he could serve her. He was sure that civilized life could be re-established only by the united efforts of all Russians.

Professor Einstein, overhearing his remarks, commented: "I agree with the Professor; a man can act no differently." Within three years, however, both Ipatieff and Einstein left their native countries for the United States.

About this time it was determined that there was a possibility of developing a process in which all of the phosphorus employed in a given experiment would be completely converted into pure phosphoric acid. The results were remarkable: he and Carl Freitag, graduate assistant of the Technological Institute of Charlottenburg, were able to oxidize phosphorus into phosphoric acid at about 300°C. and to obtain pure hydrogen without any phosphines. Dr. Caro, head of the Bayer plant, was exuberant. He told Ipatieff that I. G. Farbenindustrie was greatly interested in the process since they had bought a patent from a Swedish engineer for the oxidation of phosphorus, but the acid obtained was impure, containing the lower acids, and the hydrogen produced required purification from phosphines.

In mid-October, Ipatieff went abroad again, this time with a delegation of Soviet scientists to attend the centennial celebration of the birth of Marcellin Berthelot (1827–1907) in Paris. For the first time since the war German scientists were invited to attend a French celebration, and for this occasion Germany sent the greatest in German chemistry, Willstätter, Wieland, Haber, and Nernst. Ipatieff renewed his acquaintance with them, and for the first time met Paul Sabatier, then seventy years old.

Ipatieff accepted an invitation to attend the International Congress of Pure and Applied Chemistry held at The Hague in 1928, and from there went to Strasbourg. His report to the Congress on Industrial Chemistry was scheduled for the final session at which Raymond Poincaré (1860–1934) was to be present. Speaking in French, Ipatieff summarized the development of his basic ideas on hydrogenation under pressure which had resulted in the production of liquid fuels from coal and heavy oils as developed by Bergius and by the I. G. Farbenindustrie.

During this meeting it was announced that the French Society of Industrial Chemistry had awarded Ipatieff the Berthelot Medal.

During the year Ipatieff made several trips to Essen to test a special gasproof fabric which could be used in making clothing for the army. In the days when Ipatieff was concerned with the manufacture of phosgene he was impressed with the work of E. I. Spitalsky (professor of chemistry at Moscow University) on the

various methods for the synthesis of phosgene. He found Spitalsky's advice on chemical problems, gases, gas masks, science industry invaluable, and in time Spitalsky was made Ipatieff's assistant in his various activities for the U.S.S.R. Spitalsky was quite critical of the government, and since he had worked hard to develop poison gas preparations he disliked abandoning this field. With great consternation Ipatieff learned, in 1929, that Spitalsky had been arrested. It was incredible to Ipatieff that such a valuable and talented man, who had worked incessantly for the good of the U.S.S.R., could be charged with any criminal activity. Following Spitalsky's arrest rumors circulated in Leningrad that many other important men in the chemical industry, including Ipatieff, soon would be arrested.

When the names for the Twelfth International Power Congress to be held in Berlin on June 30, 1930, were announced, Ipatieff's was not among them. He was sent, however, as a replacement for one of the Communists. On the threat of otherwise refusing to go to the Congress, he managed also to obtain a passport for his wife.

Since Ipatieff had become increasingly aware that freedom of scientific thought in the Soviet Academy would be restricted and that academicians would be publicly criticized for their scientific labors, he and his wife left Russia early in 1930. He could not free himself from the sad feeling that he would never again see his beloved country, his beloved Leningrad, and those laboratories in which he had spent the happiest hours of his life.

THIRD PERIOD, FROM 1931 TO 1953

It has been suggested that the life of Ipatieff reads like a tale from the Arabian nights. Under the tsarist regime he became an honored and wealthy Russian. He was richly rewarded by his scientific endeavors, but the Revolution took everything from him except his knowledge and scientific skill. Under the Soviet regime he again rose to outstanding recognition. The loss of freedom made him practically an exile from his country at the age of sixty-two, while working on chemical processes in Germany. A year later he came to the United States and in this country, not then too friendly

to one of his nationality and with whose language, habits, and customs he was quite unfamiliar, he started to build again.

In the United States Ipatieff³ successfully continued his scientific work in the research laboratories of the Universal Oil Product Company, (Riverside) Chicago, Illinois, where he came to be considered "the foremost expert in catalytic reactions in connection with petroleum refining." After strenuous work in the laboratory, Ipatieff, at the age of sixty-four, took lessons in English. His success in his newly adopted land is scientific history.

Before coming to the United States from Russia Ipatieff had accomplished more than most men do in a lifetime, having served both the tsarist and the Soviet regimes; each had awarded him its highest recognition. Among his achievements are the early recognition of the catalytic principle, invention of high pressure processes, and outstanding work on dehydration. One of his most revolutionary discoveries was the alkylation of paraffins with olefins, which was thought to be impossible. This reaction along with catalytic dehydrogenation, isomerization, and polymerization made possible the high octane gasoline and the synthetic rubber so vital in war and peace.

As the years went by, Ipatieff applied his favorite processes, his catalysts and his promoters, more and more to the field of petroleum. The great developments in the petroleum industry in the last few decades, together with the triumph of modern internal combustion engines, have been due to the work of thousands of different scientists and engineers. However, if one were to select one man who more than any other was responsible for these developments, one would cite the discoveries, the genius, the development, and the indefatigable energy of Ipatieff.

In the United States Ipatieff enlarged upon his original discoveries of hydrogenation and dehydrogenation. In polymerization he continued his work on the changing of gases, which were too volatile for motor fuels, into liquids capable of being used. He extended his work of alkylation in the field of isomerization, and the application of his catalysts and promoters to cyclization in order to produce new products and more efficient fuels.

His work in the United States is further characterized by the

discovery of the "solid phosphoric acid" catalyst for the polymerization of olefins, for the discovery of the alkylation of olefins by isoparaffins, and for work on the isomerization of alkanes.

Early in the work of polymerization of olefins it was realized that the less reactive olefins are accelerated by the presence of more active olefins. For example, pure alpha butylene was not polymerized by a weak catalyst under certain experimental conditions, whereas a commercial sample of butylenes containing 30 per cent of isobutylene mixed with alpha and beta butylenes was polymerized by the same catalyst to the extent of 50 per cent under identical experimental conditions.

By the use of the "solid phosphoric acid" catalyst Ipatieff and co-workers were able to obtain gasoline from ethylene and to convert gases from the cracking process to high octane fuel. Ipatieff conducted many experiments on the polymerization of propylene and other olefins in the presence of so-called "solid phosphoric acid." Mixing phosphoric acid with various substances permits the preparation of contact masses rich in phosphoric acid which are solid at the temperature at which polymerization of propylene and other olefins occur.

In 1938, in order to pursue purely academic research more easily and to be able to teach his techniques to students, Ipatieff established (with the support of the Universal Oil Products Company) the Ipatieff High Pressure Laboratory at Northwestern University. His interest in this work may be seen from the fact that he donated \$26,000 toward this research laboratory. He also established a trust fund of \$35,000, the interest from which after his death would be used for prizes in chemistry, to be awarded under the jurisdiction of the American Chemical Society to students in chemistry in any country, irrespective of creed or race.

Evans' account of Ipatieff's connection with Northwestern University is quite interesting and is recounted below:

In July 1931, Dr. Egloff called at my home, and he had with him a tall, dark, distinguished looking man that he introduced as Dr. Ipatieff. Now, fortunately, I had heard of a Russian chemist called Ipatieff, who had done a great deal of work on high pressure

catalysis. In my ignorance, I imagined that the Ipatieff whose work was familiar to all chemists had been dead many years, and so I said to Dr. Egloff, "But surely this is not Ipatieff?" Egloff bowed not too gracefully, and said, "Yes, this is the great Ipatieff."

Because of that visit I was instrumental in having Northwestern University take him on the staff. This was not any easy task, for Ipatieff was just an unknown Russian as far as the president and board of trustees were concerned. But I accomplished my task, and when I cash in, and they see fit to enumerate the little things I have been able to do, I hope they say, "He brought Ipatieff to Northwestern University." This will be glory enough for me.

In 1940 a committee of American scientists awarded Ipatieff (for his achievements in chemistry) the highest and most coveted of American prizes, the Willard Gibbs Medal. Russia should feel especially proud of this award because up to that time it had been given to only three European scientists: Arrhenius (1911), Curie (1921), and Willstätter (1933).

Beginning his career in the United States at an age when most men retire, Ipatieff published thereafter about 150 scientific papers and obtained more than 200 patents. He had already published some 200 papers before he left Russia.

Of all the compliments Ipatieff ever received, he indicated that none pleased him as much as the one from the late Homer Adkins, who stated that: "There is no chemist in the world today who has been so productive over so long a period of time as yourself. Neither time nor place nor political nor economic conditions has stopped the flow of your creative and fruitful work in chemistry."

During his long and fruitful career many honors came to him. He was elected a member of the Academy of Sciences, in both Russia and America (the only man to have held regular membership in the National Academies of both the U.S.S.R. and the United States), he received an honorary Doctor of Chemistry degree at St. Petersburg University, Doctor Honoris Causa at the German University of Munich and at the French University of Strasbourg, and was elected Honorary Member of the Deutsche Chemische Gesellschaft and of the Göttingen Academy of Science. The French Government made him Commander of the Legion of Honor; he was the recipient of the Berthelot Medal in France; of

small and large prizes of A. I. Butlerov of the Russian Academy of Sciences. After the revolution he became President of the Central Chemical Bureau in Moscow and was the founder of the High Pressure Research Institute in Leningrad. For this valuable work he received the Lenin Prize. His book entitled "Catalytic Reactions at High Pressure and Temperature" outlines the work on catalysis in which he specialized.

In reference to his own life Ipatieff said:

I have lived a long and busy life; I have had contact with a very large number of people of all types and all occupations; I have lived through several wars and revolutions; and I cannot say that fate has been unkind to me. I am happy that in my later years, despite the troublesome times through which I have lived, I have kept my love for my chosen science, and that I still retain my physical strength. And I am most happy that I can spend these later years in this wonderful country where I have found so many talented assistants and friends.

Ipatieff was a man of charm and kindness who enjoyed social contacts. He was always ready with encouragement and assistance to anyone interested in advancing science. He was an indefatigable worker who set himself a hard schedule, any disturbance to which upset him.

Several months before his death the Universal Oil Products Company entered into negotiations with Northwestern University to establish the Vladimir Ipatieff Research Professorship by which the company grants the university \$25,000 annually for the salaries of a professor and an assistant and for other expenses. It was the source of much gratification that Ipatieff had been notified of the final details of this professorship, a few days before his death on November 29, 1952. His wife, Barbara, with whom he had celebrated their sixtieth wedding anniversary, survived him but a few days and died on December ninth.

NOTES AND REFERENCES

- 1 Evans, Ward G., *Chem. Eng. News*, 25, 3720, December 15, 1947.
- 2 Ipatieff, Vladimir N., "The Life of a Chemist, Memoirs of V. N. Ipatieff," Stanford University Press, 1946. Background cited in the first and second

period of this biography was obtained from this reference, edited by Xenia J. Eudin, Helen D. Fisher, and Harold H. Fisher. (Permission to use this material was granted by Stanford University Press by letter dated February 18, 1959.)

3 "Catalytic Reactions at High Pressures and Temperatures," Macmillan, New York, 1936.

4 *Time*, January 10, 1937.

CARL B. MARQUAND

HELEN H. MARQUAND

.. 91 ..

Fritz Haber

1868-1934



HABER'S scientific spirit was not contemplative in nature. He loved science and lived for it, not merely for its own sake, but because he affirmed its molding influence on human life. He served science because he believed it held a key position in the domains of culture and civilization. Imbued with the necessity of research for the preservation of our existence, he saw no degradation when science was applied to technical problems, and he certainly regarded pure science as being but little higher than applied science. He measured each with its proper scale of values.

The versatility of his talents and proclivities could have been a danger to his career. However, the success of his life and the benefits it brought to his fellow men were due to his ability in his youth to concentrate on factual accomplishment. Who can determine now whether it was chance, external circumstances, or internal predilection that led him to specialize in chemistry? In later years, he often left the impression that he would have been just as pre-eminent in other lines. He tried himself out in other directions but remained true to chemistry.

Born at Breslau on December 9, 1868, Haber started his scientific activity as an organic chemist. After studying at Berlin under A. W. Hofmann, at Heidelberg under Bunsen, and at Charlottenburg under Liebermann, he took his doctorate at Berlin with an organic thesis. Later he worked at Jena under Ludwig Knorr in a field that was completely in the interest of the older man, and they published a joint paper on diacetosuccinic ester. He put down no roots, however. The clarification of chemical structures and the working-out of syntheses, which constitute the bulk of organic chemistry, could not satisfy his scientific imagination. His main interest lay always in the material side of Nature and its diversity. He consistently considered himself to be a chemist and freely acknowledged this even in later years when developments brought him frequently into purely physical problems. Once when one of his younger colleagues brought up the matter of changing from chemistry to physics, he jokingly said: "As a matter of fact, the

most interesting thing in physics is chemistry." In his opinion, the art of the organic chemist was not sufficient to enable him to penetrate as deeply as he desired into material aspects. This method of approach was too specialized to suit him and too highly developed; the possibilities of the organic chemist seemed to him to be as foreseeable as those of a mature man. In comparison, what great potentialities were present in the then young field of physical chemistry which, in the hands of van't Hoff, Arrhenius, and Nernst, was in those years disclosing very remarkable, fruitful, and novel methods of attacking chemical problems?

In 1894, Haber was offered an assistantship at Karlsruhe by Hans Bunte, professor of chemical technology. He accepted because the post offered him two things that he was seeking; the professional responsibilities and connections which it entailed were welcomed by Haber. He once said that he would not have been satisfied with a research position without obligations; he wanted to make himself useful and to fit himself in, and thus get the feeling of belonging to a solid scientific group.

However, the official duties of this post were not so demanding that he did not find time for extending his scientific depth and production. Teachers who might have advanced him in his special field of interest, physical chemistry, were not to be found at Karlsruhe. Bunte's special field was combustion chemistry, particularly gases; Carl Engler was also there, but he was interested in petroleum and the phenomena of autoxidation. The problems with which Haber came in contact at Karlsruhe had a decisive influence on his later scientific investigations, and during the last years of his life he repeatedly returned to the problem of the combustion phenomena in gases and of autoxidations.

It was only two years after he became assistant that he qualified as Privatdozent with the habilitation essay "Experimental studies of the decomposition and combustion of hydrocarbons." Apart from its technical importance, the question of the mechanism of the decomposition of the hydrocarbons offers, even at the present more advanced state of our knowledge of reaction kinetics, something of special interest and is still the subject of serious researches in many countries. It is well to recall that Haber was the first to carry out well-planned studies in this field and recognized the essence of

several aspects of these problems. After another two years he published his textbook "Technische Elektrochemie." It was based on the lectures he gave at the Technische Hochschule, and it reveals the intensity with which Haber had attacked this field in which he had hardly begun to publish. The intention, expressed in the preface, to establish a contact between the most recent researches and the industrial practices which up to then had developed with almost no attention to such studies, can be regarded in an extended sense as the basis of his entire life work. That same year he reported to the meeting of the *Bunsengesellschaft* on a major experimental study of electrolytic reduction. Here he succeeded in showing that order could be brought into the bewildering maze of organic cathode processes if attention were paid to the potential at the cathode, and that definite reduction products result if the electrode potential is kept constant. The manner in which nitrobenzene is reduced in stages at the cathode was thus clearly set forth and became the prototype of a number of similar reduction processes.

The next ten years saw a host of electrochemical researches joined to the initial excursion into this field. Only a few can be cited here. The continuation of the study of electrolytic reduction reactions of organic compounds led him to the general realization that the velocity of chemical reactions at the electrodes is not infinitely great, but rather true chemical reaction rates prevail just as in homogeneous reactions. He advocated this view, which everyone shares now, in opposition to the then modern notions about the course of such reactions. In this connection he studied, among others, the establishment of the quinone-hydroquinone equilibrium at the cathode, and through this research laid the foundations of the quinhydrone electrode as developed by Bijlman, which has become a useful instrument to obtain accurate data regarding the acidity of a liquid. He himself created an instrument for the same purpose that was at least as good, namely, the glass electrode which was developed in conjunction with Cremer. It has the advantage that nothing need be introduced into the liquid being tested except the indifferent glass material and, consequently, it now finds wide use in factory operations as well as in research. This discovery was intimately connected with a group of studies, in which Haber

made the first experimental investigations of the potential differences that arise between solid electrolytes and their aqueous solutions, and in which he found laws similar to those that apply to the contact of metal solutions. These observations are of much physiological interest, since the bioelectric systems show greater similarity to the Haber elements than to the usual galvanic cells with their metal electrodes. In addition to the electromotive behavior of the solid electrolytes, studies were made of their conduction characteristics, and for the first time there was detected an electrolysis of a solid crystal of salt in accord with Faraday's law.

However, another fundamental problem of electrochemistry occupied Haber even more during these years. When steam engines, turbines, and motors are driven by fuels, a large part of the energy is inevitably lost. The theories of physical chemistry indicate how a combustion process can be guided by electrochemical means so that the loss of energy is limited to the physically necessary fraction. But the construction of such so-called reversible fuel elements encounters great difficulties. Haber spent much work on this topic, which is one of the cardinal problems of industrial physical chemistry, and he succeeded in finding at least the fundamental solution for the laboratory combustion of carbon monoxide (and also hydrogen) even though the road to the commercial application remains difficult.

His interest in electrochemical problems gradually receded, and two problems from gas chemistry claimed more and more of his attention. These were the elucidation of the combustion processes in flames and the fixing of the nitrogen from the air. Haber's investigations of the Bunsen flame have become fundamental to an understanding of the processes occurring there. By chemical analysis of the gases, which he drew off from the region between the inner cone and the mantle of the Bunsen flame, he demonstrated that in the luminous inner cone there is established the thermodynamic water gas equilibrium, whose temperature can be calculated from the composition; a combustion of water gas takes place in the outer mantle. These studies then led to a chemical method of determining flame temperatures which, when direct measurements are possible, agree very well with the latter.

As at the start of his electrochemical researches, Haber at the

beginning of his studies of gas reactions published a monograph. His fundamental text on "The thermodynamics of technical gas reactions" appeared in 1905. The foreword stated that the book was written from the industrial rather than the theoretical viewpoint. Nevertheless, it is a model of scientific rigor and thoroughness, which in its treatment of the so-called thermodynamically undetermined constants led directly to the door of the Nernst heat theorem. In this book there are appraisals of the approximate position of the ammonia equilibrium on the basis of observations which he had made the preceding year. At 1000°C ., with the aid of iron as catalyst, small amounts of ammonia were produced from N_2 and H_2 . A new approach to the fixing of atmospheric nitrogen was thus indicated, but the yields were so hopelessly low that Haber did not choose to follow this road. Yet the problem gave him no rest, and he spent several years studying the then customary method of oxidizing nitrogen by electrical arc discharges. It was not until 1908, when he became better acquainted with the possibility of working on an industrial scale under high pressures, and after more exact data were made available to him by others regarding the position of the ammonia equilibrium, that he became convinced, in the face of the skeptical opinions of all the experts, that the method of the future lay in the synthesis of ammonia. Together with Le Rossignol he made a systematic search for good catalysts and, when these had been found, built a small model with which, in June, 1908, he was able to demonstrate to the industrialists the synthesis of ammonia on the laboratory scale.

The consequences of this exploit were stupendous in comparison with what was foreseen at the time. In the hands of Carl Bosch, there arose in the next few years the great Oppau and Leuna ammonia works, which first of all provided Germany with the raw materials for munitions in World War I and then, after peace had come, furnished the means for making the soil more fruitful and remunerative. The principle employed in the ammonia synthesis proved to be of use in other important technical processes, and the further development, namely, the art of controlling catalytic reactions at high pressures and temperatures, made possible the synthesis of methyl alcohol by Alwin Mittasch and the hydrogenation of coal by the Bergius method.

The years just preceding World War I saw a change in the structure of physical chemistry. The period of classical physical chemistry appeared to be passing. The thermodynamic problems, so far as they related to chemical equilibrium, seemed to have been brought to a certain degree of conclusion by the Nernst theorem, and the first victorious dawning of the quantum ideas in energetics and atomistics were making their appearance. With these it was possible to gain a deeper insight into chemical equilibria with the aid of statistical methods, as shown by the calculation of chemical constants, and also to approach closer to the chemical events themselves. It is interesting to note a parallel turning toward atomistic problems in Haber's studies. The problems which Haber pursued were invariably the questions of his time. He lived in the present, he did not become rigid, and he shared the interests of the constantly renewed younger generation. Accordingly, his scientific work was a mirror of the development of physical chemistry during his adult life, and the influence which he exerted was founded on his scientific successes as well as on the prestabilized harmony between his own development and the spirit of his time.

Among the experiments leading into the new epoch are the study of the ion emission of platinum wires during the course of catalytic reactions, and the proof that electrons can be sent out during certain chemical reactions.

In this sense, it is more than chance that the first paper of the transactions of the Kaiser Wilhelm Institut für physikalische Chemie in 1911 is a paper by Fritz Haber dealing with the ultra-violet and infrared natural frequencies of crystals and the relation between chemical heat effects and energy quanta. Although the findings of this study, except for an interesting empirical relationship for the crystal's natural frequencies, were later superseded, because the questions dealt with were not mature enough at the time, the study nevertheless shows that a completely new set of problems had gained entrance to his world of ideas, problems which were to have a part in determining the nature of the work carried out in the laboratory of which he had become the director. However, it was eight years before he again took up a portion of these trains of thought and followed them through to a conclusion. The few years preceding the war were occupied by getting the Institut into

running order and no new fundamental studies were begun. In the main, the ammonia synthesis was further developed from the quantitative standpoint. Three things, however, are worth mentioning: (1) for mining: the invention of the firedamp whistle; (2) for laboratory practice: the development of a quartz thread manometer for low gas pressures; and (3) for chemical detection: the observation that the adsorption powers can be due to unsaturated valence forces of a solid body. Langmuir built his adsorption theory on the latter finding.

Then came the war and with it an interruption of the scientific output; this was destined to have a serious effect on Haber himself. This is not the place to discuss in detail Haber's activities during the war. At the start he was attached to the Ministry of War as a consultant and later was given an independent section. He developed the first gas attack procedures and later organized the entire gas warfare and gas defense. Eventually this organization included 150 university personnel and about 2000 assistants. The Kaiser-Wilhelm-Institut für physikalische Chemie became the center for the necessary investigations. In addition, Haber advised the Ministry with respect to the most varied problems regarding raw materials and industrial matters. It was an overpowering burden, and he paid for it in terms of his health.

When the collapse of the German resistance and economy came in 1918, he did not immediately return to pure research activities. Rather he sought to devote his organizational and technical abilities to the restoration of the stricken nation. The great commercial success of the ammonia synthesis, his activities during the war, and the bestowal of the Nobel Prize (1918) had brought him so much respect that he was in demand everywhere. He took a prominent part in the creation of the great relief organization *Notgemeinschaft*. He accepted the chairmanship of large scientific societies and battled with skill and success for the recognition of German representatives in international organizations. He worked particularly on the effort, planned by him, to set up an elaborate undertaking to recover the traces of gold that were alleged to be in sea water. He expended much time and thought on this from 1920 to 1926. These studies ended in practical failure, a result that wounded Haber seriously. Already somewhat weakened in health,

the shattered hopes of thus enabling Germany to meet its war reparations were ascribed by him as due to his decreasing efficiency, and he was deeply depressed. But, driven by unrest, he soon found another field of activity.

The reorganization of the Institut was his first concern after the war. He succeeded in enlisting prominent scientists as collaborators in this research center and, thanks to the quality of his leadership and despite the many difficulties, in a few years it was one of the best institutions of its kind in the world. The most varied types of work were nurtured by him but conducted in completely independent fashion. The constantly increasing number of publications testified to the healthy growth of this establishment. The fundamental studies by James Franck and his associates on the electron bombardment of atoms were published in the years immediately following the war. Here could be discerned the essence of chemiluminescence and the nature of the photochemical primary processes. Our ideas of the primary fission products of molecules when struck by electrons were greatly enriched by the investigations from this laboratory, and almost all that was known up to the time of Haber's death regarding the chemistry and reaction kinetics of the free metalloids and metal atoms came from his laboratory. The resonance phenomena due to collisions of certain molecules were here given their first clear experimental proof. New kinds of molecular absorption spectra, which represent a transition to x-ray absorption spectra, were found in the extreme ultraviolet. The predictions of quantum mechanics were confirmed by the discovery of parahydrogen. Measurements were made of the life span of atoms in various states of excitation. Information about the constitution of atoms was obtained from studies of hyperfine structures. The chemistry of silicon was extended by the discovery of a new group of most unusual compounds. Nowhere else in Germany was more done to advance colloid chemistry. The whole multiplicity of colloid phenomena was disclosed in these researches. Fundamental studies of the electrokinetic potential and its relation to the thermodynamic electrical equilibrium potential were made here, and the significance of the former with respect to the flocculation of colloid systems was investigated experimentally. Special interest was given to the shape of the colloid particle and to the structures in gel and

sol form. This problem was attacked by mechanical, optical, and magnetic methods and yielded many surprising findings as the result and expression of these structures. Nor did these investigations neglect the problems of colloid chemistry encountered in biological and industrial fields.

And what was Haber doing during this development of the Institut? He by no means exhausted himself in caring for the material and organizational needs or in collecting the necessary funds. Rather, by virtue of his sovereign superiority, he held together the apparently heterogeneous and divergent tendencies within the establishment. The colloquium, at which he assembled the entire staff every fortnight, was a prime example of his guiding talent. Often, at the close of a hazy and too specialized lecture, he took the floor himself and in two or three sentences put the problem in such succinct terms that the darkness was dispelled—at least to a considerable extent. How often the audience derived more from his few sentences than from the entire preceding hour! Care was exercised that absorption in special problems did not result in the loss of proper perspectives and standards. Nothing was less welcome to Haber during discussions than indefiniteness. In order to make himself clear, he often spoke in terms of plastic comparisons, frequently only as a matter of experiment to arouse discussion when he had possibly misunderstood something. And then, with a gentle smile, he put the Socratic questions from which clarity eventually emerged from the discussion. Just as his inventive spirit made him a research man, his organizing talent made him a model director of a large laboratory. His ability to permit full freedom to the individual workers and yet to keep the mental control of the whole in his own grasp was almost unbelievable.

When, disillusioned, he had given up the attempts to recover gold from sea water commercially and thus had more time to devote to the investigations being conducted in the Institut, it was this writer's good fortune that Haber, at the close of the 1920's, turned his attention to the group in which I was the leader. The probable reason was that he saw in the results that we had obtained concerning the behavior of free atoms and free radicals the possibility of applying new methods to problems that had engaged him in his early years, the field of flames, particularly the Bunsen flame,

and autoxidations. He now reverted to purely scientific work. Although handicapped by a serious cardiac condition accompanied by painful angina pectoris, he energetically collected all of his powers, participated in our inner group colloquium, occupied himself with the theory of spectra, and again took up his old studies. It was not to be expected that decisive results would be obtained immediately by this method, but through these investigations he pointed out the way which later investigations pursued. His last researches, in 1933, dealt with hydrogen peroxide catalysis. At this point, the anti-Semitic barbarism of the Nazi regime entered the picture. He left the institute shortly after addressing the Minister (May 2) as follows:

My tradition requires of me in a scientific post that in choosing fellow workers I take into account only the professional qualifications and the character of the applicants without asking about their racial disposition. You will hardly expect a man of sixty-five to alter his mode of thought that had guided him in the thirty-nine years of his academic career, and you will appreciate that it is the pride with which he has served his German homeland through all of his life which now dictates the request for retirement.

Shortly thereafter Haber left Germany to open a small laboratory at Cambridge where he had been invited by English colleagues. He did not withstand this transplanting well, his thoughts were constantly on his homeland, his health worsened, and he feared the rigors of the English winter. Within a few months he moved to Switzerland but his spirit was broken, his health was gone. He died January 29, 1934, at Basel, an outcast rejected by the authorities of the country he had served so well.

Richard Willstätter once said: "To judge Haber by his published work would be like trying to learn about the sculptor Hildebrand from his books or about the painter Van Gogh from his letters." Although this statement is somewhat exaggerated, it contains much truth. The basic nature of scientific research is such that the individual and personal qualities of the man are subordinate to his accomplishments. However, Haber was a very forceful and unusual person. Those who knew him will never forget this personality, its memory will enrich their lives always.

The bitterness and tragedy surrounding the close of this brilliant career have yielded to the inexorable softening influences of time. A ceremonial session was held at the Kaiser Wilhelm Institut für physikalische Chemie und Elektrochemie on December 9, 1952, and an impressive tablet was unveiled to Haber's memory. The inscription reads:

Themistocles has come down in history not as the exile at the court of the Persian king but as the victor at Salamis. Haber will go down in history as the gifted discoverer of the process of combining nitrogen with hydrogen, which is the basis of the industrial fixing of nitrogen from the atmosphere, who in this way, as was stated when the Nobel Prize was conferred on him "created an exceedingly important means of improving agriculture and the welfare of mankind, who made bread from the air and scored a triumph" in the service of his country and all mankind.

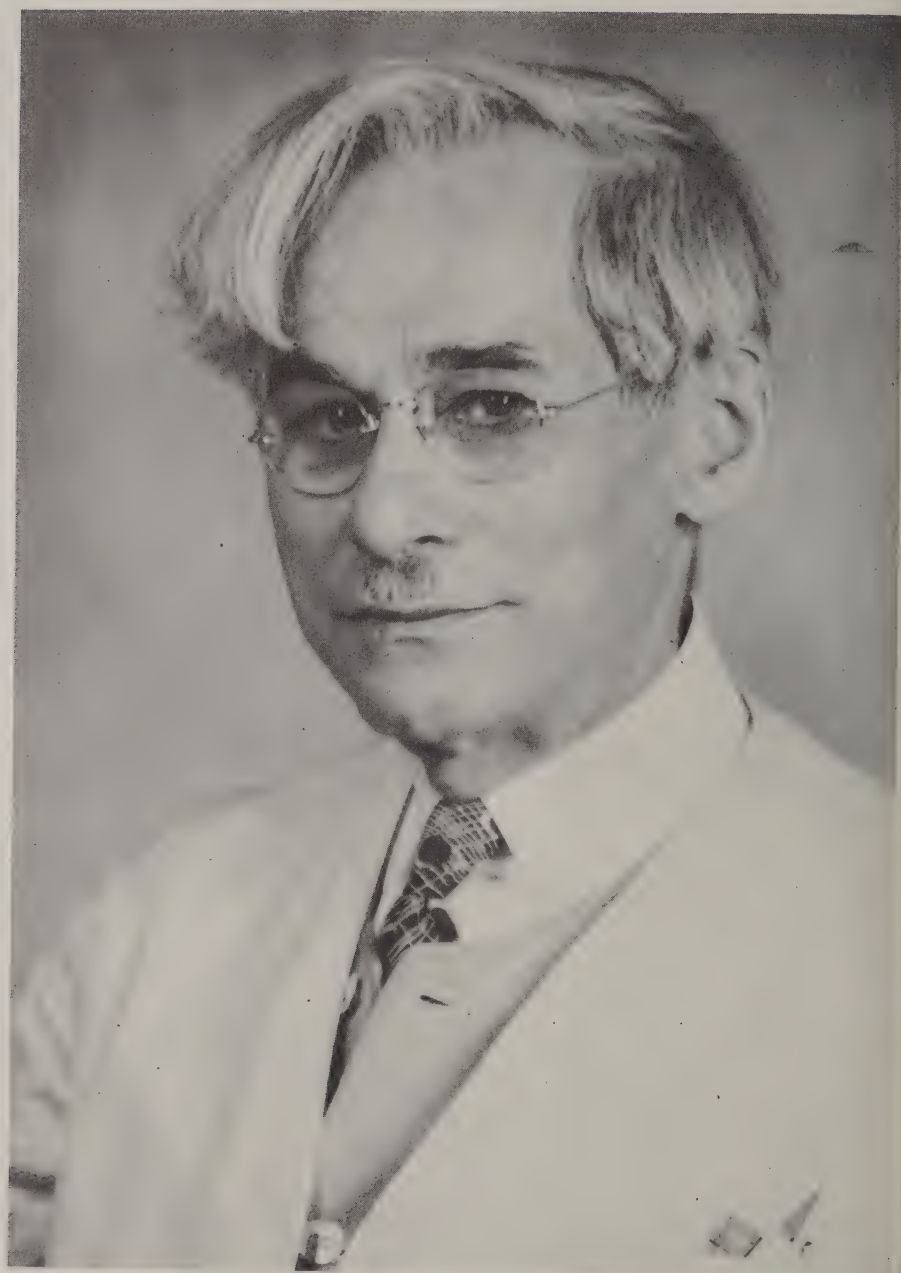
From: *Z. Elektrochem.*, 57, 2 (1953). Translated by Ralph E. Oesper.

K. F. BONHOEFFER

.. 92 ..

Phoebus Aaron Theodor Levene

1869-1940



PHOEBUS AARON THEODOR LEVENE was a great pioneer in biochemistry who arrived on the scene after structural organic chemistry was well established and after Emil Fischer had completed his work on the fundamental nature of the components (*Bausteine*) of proteins and carbohydrates. Although Levene was trained as a physician and held no other degree than that of M.D., he worked as an isolative and structural organic chemist and was not averse to applying physicochemical concepts and techniques when such were indicated. He continually read and studied, attended classes in advanced chemistry, and worked in many laboratories of Europe. He utilized well the capabilities of his co-workers. He possessed great energy and drove himself mercilessly. As a member of the first group of scientists assembled by Dr. Simon Flexner at the founding (1905) of the Rockefeller Institute for Medical Research in New York City, he contributed greatly to the establishment of biochemical research in this country. He initiated research which has been continued by veritable hosts of other workers in the universities and research institutes of the world—investigators who have found that the foundations laid by him were firm and solid.

Levene was born into an Orthodox Jewish family of Sagor, Russia, on February 25, 1869, and was named (as transliterated from the Russian) Fishel Aaronovich Levin.¹ He was the second of eight children of Aaron and Etta (Brick) Levin. When he was four years old his family moved to St. Petersburg (later called Petrograd and then Leningrad) where the Hebrew name "Fishel" was changed to the Russian "Feodor"; his family and intimate friends always called him Fedia, which is the Russian diminutive of Feodor. When he came to the United States, the name Feodor Aaronovich Levin somehow became transliterated as Phoebus Aaron Levene. Some years later, after he had realized that the proper English translation of Feodor was Theodor(e) and not Phoebus, he decided it was too late to change his name, then ap-

pearing in scientific publications, from Phoebus to Theodore. He therefore decided to insert Theodor as a third name and listed himself as Phoebus Aaron Theodor Levene (he dropped the final "e" in Theodore as such vowel endings are not found in Russian). This caused some confusion when initialed on circulars as P. A. T. and there were over-zealous clerks who decided that such abbreviations were undignified and should be changed to the proper address of Patrick Levene. All this tumult was obviated in most of his publications by adopting the simplified form P. A. Levene.

Levene's father was a custom shirtmaker and operated three stores in St. Petersburg, one of which was on Nevsky Prospect, the Fifth Avenue of that city. Fedia graduated in 1886 from the Classical Gymnasium where he was subjected to eight years of Latin and Greek—he was able later to read Newton's "Principia" in the original Latin. The eldest son, Isaac, was set on becoming a physician and was able to realize this ambition. Fedia did not have the same consuming desire to study medicine but went into it because the difficult examination for entrance to the St. Petersburg Imperial Medical Academy was an intriguing challenge to him. He passed the examination with flying colors and entered the Academy. There he came into contact with Alexander Borodin² and could recall the grief of Rimsky-Korsakov on the death of Borodin in 1887. Ivan Pavlov was docent in physiology at the time. Borodin, who had succeeded Nikolaï N. Zinin, was assisted by Alexander Dianin.³ Levene participated in some of Dianin's researches concerned with the condensation of phenols with aldehydes and ketones. This experience introduced the young medical student to chemical research and he was advised by his teachers to study chemistry further. Thereafter he leaned more toward chemistry than medicine.

Before Levene had completed his medical training, because of the growing anti-Semitism in Russia as well as to find broader opportunities and a fuller life, his family decided to emigrate to America, and the young Levene accompanied them to New York where they arrived on the Fourth of July, 1891. He returned to Russia in the fall to complete his examinations for the M.D. degree which he received in the autumn of 1891. He rejoined his family

in New York in March of 1892, passed his examinations for the profession of medicine in New York, and practiced in the Russian-Jewish colony on the lower East Side until 1896. In later years he maintained occasional contact with the remnants of this section through the Russian Bear, an authentic Russian restaurant boasting a balalaika orchestra.

Orthodox Jews and Russian medical students wore full beards, but this was shortened to a mustache by Levene, who then bore a striking resemblance to his sister Vera's husband, Morris Hillquit, with whom he shared an office. Morris Hillquit (1869–1933), later a leading socialist of this country, was then a budding lawyer. As neither could afford to lose a patient or a client, it was their custom to "bluff it out" for the other when either was alone in their mutual office.

While a medical practitioner, he enrolled at Columbia University and attended the lectures in organic chemistry of Professor Marston T. Bogert. At the same time he was given working space in the laboratory of Professor John G. Curtis of the department of physiology of the College of Physicians and Surgeons, Columbia University, then on 59th Street, from where he published, in German, his first paper entitled "Die zuckerbildende Function des N. vagus (The Sugar-Forming Function of the Vagus Nerve)." He also worked on the physiology of sunstroke, then prevalent in New York City during the summer. During the summer of 1896 he took over, in addition to his own, the medical practice of his brother Isaac Levin (Isaac had not changed the Russian form of his surname), who had gone to Europe. On Isaac's return, he found that his brother had contracted tuberculosis; after consulting an eminent diagnostician, Fedia was sent to Switzerland to recuperate. After spending a year there, which included a short term in the laboratory of Professor E. Drechsel in Bern, he returned to recuperate further in the Trudeau Sanatorium at Saranac Lake, New York. While at Saranac he utilized their laboratories for further research.

Following this period, and while still far from well, Levene decided to discontinue the practice of medicine and dedicate his life to chemical research in relation to medicine. He was appointed

"Director of the Physiological Chemistry Division of the Pathological Institute of the New York State Hospitals for the Insane," but this unit underwent some political vicissitudes. He held a position as chemist at the Saranac Laboratory for the study of tuberculosis. He studied abroad in the laboratories of Professors A. Kossel (Marburg), H. Hofer (Munich), and E. Fischer (Berlin). His name appears on a publication of E. Fischer on the analysis of gelatin by the ester method. In 1902 he returned to the chemical laboratory of the reorganized Pathological Institute of the New York State Hospitals on Welfare Island and continued there until 1905. By 1905 he had published 84 papers and had been invited to present the Herter Lectures in pathological chemistry at New York University Medical College. Those papers included his first studies on the preparation and analysis of nucleic acids, work on the chemical nature of mucins and of chondroitinsulfuric acid (*Glycothion-säure*), studies on the biochemistry of the tubercle bacillus, and on the enzymic reactions of autolysis. He therefore was well established in biochemistry in this country on the basis of a publication record, and this led to his selection by Dr. Simon Flexner for an appointment as assistant in chemistry in the newly formed Rockefeller Institute for Medical Research, where he remained for the rest of his life. In 1907 he was made a member of the Institute in charge of the Division of Chemistry. He was made a member emeritus in 1939 but continued work unabated until his death of a heart condition on September 6, 1940. On one of his periodic visits to Saranac Lake he met Anna M. Erickson, a native of the Norwegian Lutheran colony of Evanston, Illinois, whom he married in 1920 when he was fifty-one years of age. This marriage was a very happy one and Anna Levene proved to be an ideal helpmate for him. They had no children.

Dr. Levene was a thin, wiry man of short stature. He had very penetrating, dark-brown eyes, and an intense, rather stern, expression. He wore a small mustache and his head was covered with a heavy shock of hair which in later life became steel gray and which he was wont to toss about or run his hands through in characteristic fashion. He moved rapidly and loved to work in the laboratory with his own hands, assisted only by his *Diener*, Joe Lender,

whom he always addressed in German. When the writer knew him first, in 1927, Levene's routine was to rise early and read and write at home. At eight o'clock the telephone would ring on his floor and he would talk to members of his group on ideas that may have come to him regarding their work. At about 9:30 he would appear in the laboratory and plunge into experiments of his own in his neat and excellently equipped personal laboratory. After a short rest following lunch he would literally tear out of his office and make the rounds of his co-workers, after which he would resume his own experimentation. In the afternoon he would write up his notes on easily filed cards and then proceed homeward with a briefcase full of the journals which had arrived in the library that day. His summers were mainly spent away from New York as soon as his wife could pry him loose from his activities. Although he traveled widely in Europe, he never did so in the States and he held very naïve and astonishing concepts of the hinterland west of the Hudson River.

His temperament was strictly artistic. He published all of his work in the *Journal of Biological Chemistry*, established by the Rockefeller Institute group, and his manuscripts were sent to press immediately with no refereeing and little editing. Although he had numerous co-workers who provided experimental portions, he wrote all his own introductions, and I have known him to dash one off in twenty minutes, complete with references. In all he published over 700 articles. Levene spoke an excellent German and a perfect French. His English had a heavy accent, said to be Russian. One morning the writer entered Dr. Levene's laboratory to use his microscope in the customary search for crystals in a sugar sirup, and Dr. Levene maintained a running conversation simultaneously with the writer in English, with Dr. Steiger (from Paris) in French, and with Joe Lender in German, while at the same time carrying on his laboratory work on the bench. Dr. Levene directed his laboratory group with a firm hand and ordinarily brooked no suggestions from its members, unless it could be claimed that they were derived from the papers of Emil Fischer. The writer shared a double laboratory with one of Dr. Levene's collaborators who was working on configurational relationships in simple compounds in-

volving straightforward, though difficult, organic syntheses utilizing Grignard reagents and the like. With this type of technique, Levene was not overly familiar and his co-worker had an excellent method worked out. He would first try to find what "worked" and then, by adroit conversation, get Dr. Levene to suggest that he try this. The next day Dr. Levene would be delighted to find that the experiment had been quickly and successfully carried through. This method, however, was inapplicable to laboratory work, such as that with the sugars, with which Dr. Levene was thoroughly familiar in minute detail.

Away from the laboratory, as in his New York apartment, Dr. Levene could relax and become a gay and charming host. He had numerous friends about the city, and his home was the center for the gathering of many interesting groups. He maintained a keen interest in contemporary art, and the walls of his home, where not covered by the multitudinous bookcases present, were decorated with many paintings he had purchased from young artists who he hoped had a future. He was a regular attendant at the concerts of the New York Philharmonic Orchestra and also enjoyed the better theatrical productions. As might be expected, Dr. Levene held liberal views; although thoroughly pleased with the Kerensky revolution he was not in sympathy with the Bolshevik counterrevolution. His home and laboratory formed a mecca for the constant stream of refugees reaching these shores from the excesses and trials incident to the vast changes then occurring in Russia.

Levene's scientific work embraced all classes of tissue constituents and the basic chemistry related thereto. He liked to find groups of compounds susceptible to investigation by graded hydrolysis and was very successful in this. He was a master in the isolation of pure substances from complex mixtures and in the crystallization of intractable sirups. He placed great reliance on the test tube. He had little patience with micromanipulations and worked with relatively large quantities. His favorite expression, when a line of work petered out due to a lack of material, was "next time we will make a kilo!" He was ever on the lookout for new techniques or "tricks," as he was wont to call them. He introduced the Pregl organic microanalyses to this country when he brought to New

York one of Pregl's students in the person of Oskar Wintersteiner, who in turn trained Dr. A. Elek. Dr. Elek remained with Dr. Levene throughout Levene's career.

Levene's main mark was made in the structural chemistry of the nucleic acids. He defined the nucleotide and, with Dr. R. Stuart Tipson, he explored its fine structure through methylation techniques. He isolated and characterized the two sugars by which the modern biochemist classifies the nucleic acids into their two characteristic groups. Both sugars were at the time unknown. The first was D-ribose and the second was its 2-deoxy derivative (2-deoxy-D-erythro-pentose). The discovery of the first was made in 1909, but the second was not uncovered until twenty years later, although many attempts to attain this goal were doggedly made in the intervening years. This was because the deoxypentose was destroyed by the acidity required to break it loose, and the appropriate enzyme could not be found. Finally, success was obtained by passing a solution of nucleic acid through a gastrointestinal segment of a dog by introducing it through a gastric fistula and withdrawing it by an intestinal fistula. This difficult experiment was done in cooperation with the Russian physiologist, E. S. London. There followed a great rush to establish the configuration of the 2-deoxypentose but it did not fit any of the known structures quickly synthesized. Then, in 1930, a paper appeared in the *Journal of Biological Chemistry* with data to show it was "2-deoxy-D-ribose." The discrepancy was caused by the circumstance that Joe Lender had, in the excitement, mixed two bottles of D- and L-arabinose of unequal content with a consequent utter confusion in the rotatory powers of the resultant, partially racemized preparations.

Levene was a pioneer in determining the nature of those tissue constituents containing proteins, uronic acids, N-acetylhexosamines, and sulfuric acid, of which the main member is chondroitinsulfuric acid from cartilage. He found that the hexosamine component of this substance was then unknown 2-amino-2-deoxy-D-galactose (its exact 2-epimeric nature was not established until later by others). He was much intrigued with the D-galactose-containing components of the brain and nervous tissues and carried out significant work in the isolation and characterization of these cerebroside. The struc-

ture of several of the important sugar phosphates, of significance as intermediates in alcohol fermentation and in carbohydrate metabolism in tissues, was elucidated with Albert L. Raymond. In the protein field, he presented evidence in favor of the linear polypeptide theory of protein structure.

Requisite to the sugar work in relation to tissue constituents, the Levene laboratory carried out an enormous amount of experimentation in fundamental carbohydrate chemistry. The synthesis and reactions of the hexosamines were studied and several were described for the first time. With Walter A. Jacobs, he synthesized the new hexoses D-allose and D-altrose and their aldonic acids, through the cyanohydrin reaction on natural D-ribose.

In attempting to determine the configuration of the second carbon in the hexosamines, Levene encountered the puzzling phenomenon of Walden inversion. In an attempt to solve the question of when or when not does a Walden inversion occur, he carried out a series of masterly investigations on the configurational relationships in a group of simple structures synthesized by methods obviating the possibility of Walden inversions. This work was done mainly with H. L. Haller and R. E. Marker and, while it did not solve the problem of Walden inversion, it did lead to the establishment of reference substances which have been of great value to later investigators.

It is obvious that the above summary does not do justice to the some 720 publications of P. A. Levene and his co-workers, but it is hoped that it has delineated some of the high lights in the picture. Levene was a member or fellow of the American Association for the Advancement of Science, the American Chemical Society, the American Philosophical Society, the American Physiological Society, the American Society of Biological Chemists (charter member), the American Society of Naturalists, Bayerische Akademie der Wissenschaften, Deutsche Akademie der Naturforscher (Halle), Deutsche chemischen Gesellschaft, the Harvey Society, the National Academy of Sciences, the Royal Society of Science (Sweden), Société de chimie biologique, Société chimique de France, Société Royale des sciences médicales et naturelles de Bruxelles, Société Suisse de Chimie, the Society of Experimental Biology and Medicine, and Phi Lambda Upsilon (honorary mem-

ber). He was awarded the Willard Gibbs Medal of the Chicago Section of the American Chemical Society in 1931 and the William H. Nichols Medal of the New York Section in 1938. Levene was quite proud of the fact that he had never served on a committee nor held an office in any society, and in general he was impatient with what he considered to be the lack of scholarship and culture exhibited by most of the members of the American scientific societies of the time. He did enjoy the symposia of the Organic Division of the American Chemical Society and occasionally attended meetings of the National Academy. He encouraged his younger co-workers to attend meetings, especially those of the American Chemical Society.

The stature of P. A. Levene as a pioneer of modern biochemistry increases with time. His rapid and piecemeal publication in so many fields was bewildering to his contemporaries and made his work very difficult to follow in its entirety. He trained many men, most of whom entered the expanding field of biochemical research then being established in the research institutes, hospitals, and government laboratories of the country. He always stood behind his men and spent a great deal of time in aiding them to obtain suitable positions. Very few of his co-workers became established in the American universities. This is perhaps to be ascribed to the rather aloof attitude toward the universities adopted by the Institute (or perhaps it was the reverse). The Rockefeller Institute and the Rockefeller Foundation, whose leaders stemmed largely from the Johns Hopkins Medical School, cooperated with Johns Hopkins in revolutionizing medical training and medical research in this country. They set a pattern and were successful in doing so. In this effort Phoebus A. Levene made his sterling contribution. The award of the Willard Gibbs Medal in 1931 was made to P. A. Levene as "the outstanding American worker in the application of organic chemistry to biological problems." That citation is one which will go unchallenged for many years to come.

NOTES AND REFERENCES

- 1 The writer is indebted to Dr. Levene's youngest brother, Alexander, for much information regarding the early life of P. A. Levene.

- 2 Alexander Porfirievich Borodin (1834–1887). Professor of chemistry at the St. Petersburg Imperial Military Academy; organic chemist and famous Russian nationalist musical composer; introduced coeducation into the Russian universities.
- 3 Nikolai Nikolaevich Zinin (1812–1880). Established the reduction of nitrobenzene to aniline; discovered azoxybenzene.

D. D. Van Slyke and W. A. Jacobs, "Phoebus Aaron Theodor Levene," *Biographical Memoirs, National Academy of Sciences of the U.S.A.*, XXIII, 75–126 (1944); R. S. Tipson, "Phoebus Aaron Theodor Levene," *Advances in Carbohydrate Chem.*, 12, 1–12 (1957).

MELVILLE L. WOLFROM

.. 93 ..

Fritz Pregl

1869-1930



IN THE beginning of our century, when organic chemists began to increase their work on the chemistry of special substances which are active in the organisms of plants and animals, the quantities of these substances that could be obtained were often extremely small. Thus, the problem of carrying out elementary analyses with the smallest possible quantities of a substance became more urgent from day to day. In his own research on the constitution of specific acids obtained from gall, Pregl in 1909 obtained such a tiny yield of a cholic acid derivative that he was confronted with the decision as to whether to abandon further studies of this compound or to start with such large quantities of bovine galls that the expenditures in time and cost would have become excessive and unbearable. In this dilemma, he decided to follow a new path which led him to the quantitative microanalysis of organic substances, an almost virgin field. His decision to elaborate micromethods of elementary analysis may have been facilitated by the fine success achieved by Friedrich Emich (1860–1940) at the Technische Hochschule in Graz. At about that time, Emich had shown that working with small quantities of substances is fundamentally reliable and advantageous. This method was especially congenial to Pregl's gifts and interests. He was a man of painstaking skill which enabled him to carry out difficult work in glass blowing. He had also demonstrated his great skill as a young physician, when he acted as an eye doctor during vacations and performed many a difficult surgical operation. In addition, Pregl had spent several years on improving the methods of elementary analysis. He constructed a time-saving automatic combustion oven for determining carbon and hydrogen in organic substances.

When he started his microanalytical research, Pregl recognized immediately that he needed an exceptionally sensitive microbalance. In Emich's laboratory he had seen the assay balance built by W. Kuhlmann of Hamburg for precious metals. He discovered that this balance, which can be loaded with up to 20 grams, was capable of much greater precision than claimed by Kuhlmann,

provided it was treated and handled right. The guarantee stated an accuracy of 0.01 to 0.02 of a milligram but Pregl showed how to use it for weighing to plus or minus one-thousandth of a milligram.

Within two years of work, Pregl succeeded in reducing the quantity needed for an elementary analysis to about one-fiftieth of the usual amount. In a lecture with experiments before the German Chemical Society in Berlin on February 27, 1911, he demonstrated for the first time that the quantitative analysis for carbon, hydrogen, nitrogen, sulfur, and the halogens can be carried out using only 7 to 13 milligrams of a substance.

During the following years, Pregl improved and simplified the micromethod for determining the most important elements in organic compounds so far that only 3 to 5 milligrams was necessary, and the accuracy was the same as with the usual macroanalysis. In a lecture at the scientists convention in Vienna, 1913, he demonstrated to his audience that the molecular weight and composition of an organic substance—he used acetanilid—could be determined in one hour. Thus he aroused a wide interest in organic microanalysis. From that time on, increasing numbers of chemists came to Pregl's laboratory to learn the methods from the master himself. He liked the personal contacts and introduced many colleagues to microanalytical methods, first in Innsbruck and later in Graz. These occasional instructions developed into regular courses, held several times a year and attended by hundreds of chemists from all over the world. The author of this biography continued these courses at the Pregl Laboratory after Pregl's death in 1930 and as his successor until 1938; they were resumed after international relations were restored in 1949. After Pregl had seen that the procedures worked not only in his laboratory, but had proved successful for years at other institutions, he published his experimental results in a book on quantitative organic microanalysis (*"Die quantitative organische Mikroanalyse,"* Berlin, Julius Springer, 1917). New editions appeared in 1923, 1930, 1935, and 1947, the last two under the care of Hermann Roth. The book was translated into several languages.

Recognition of Pregl's great achievements did not fail to come soon. In 1914 the Vienna Academy of Sciences awarded him the

Liebig Prize in chemistry. The University of Göttingen gave him an honorary degree in philosophy (1920) stating: "Pregl has thought out the methods of organic microanalysis, and he has completed them in undefatigable work. He has thus greatly promoted applied chemistry and has enabled medicinal chemistry to solve new tasks." The highest recognition and honour was the Nobel Prize in chemistry in 1923.

Thanks to the pioneering work of Fritz Pregl, the further progress in quantitative organic microanalysis was rapid. There are chemists who feel that this was the most significant advance in organic elementary analysis since Liebig's times.

In 1930 Pregl donated a substantial sum of money to the Vienna Academy of Sciences for the purpose of establishing a Fritz Pregl Prize in microchemistry, to be awarded, if possible annually, to Austrian microchemists.

In the years since Pregl's death microchemistry has advanced and expanded in all special fields of chemistry. Elementary analysis has been further enriched by the microanalytical procedure for oxygen determination according to Schütz-Unterzaucher. Automatizations and simplifications have been developed in the laboratories of industry. Further refinements and work with still smaller quantities of substance have been achieved. Thus, Unterzaucher succeeded in reducing the quantity required for the measurement of carbon, hydrogen, and nitrogen to a few tenths of a milligram and still obtain reliable results.

The development of microchemistry and the increased number of publications in this field made it appear desirable to establish a new journal in which the new experiences of working with smallest quantities could be brought together and made available to the microchemists. R. Strebing in Vienna prepared the steps leading to such a publication. Under his editorship the first volume of *Mikrochemie* came out in Vienna, 1923. The size was rather modest at first. Since 1929, the staff of editors was expanded by including several outstanding microchemists, among them Emich and Pregl, and now the journal has grown in size and has an international readership.

Pregl's life and development was that of a scientist who made his own way. Born September 23, 1869, the son of an official at

the savings bank of Krain, Fritz Pregl attended the German gymnasium there. After the early death of his father, he moved with his mother to Graz and there began to study medicine in 1887. As a student he far exceeded the average. Consequently, the physiologist Alexander Rollett made him an assistant even before he had completed his studies. Pregl remained in this position, which he liked very much, for fourteen years. He became doctor of medicine in 1894, Privatdozent in physiology five years later. At that time he also studied chemistry, stimulated by his friendship with Zdenko Skraup (1850–1910) who was then director of the chemistry department. This was of decisive influence on his later career. His work on acids obtained from gall, called cholic acids, gradually led him almost completely into chemistry. After the death of A. Rollett in 1903, Pregl gave the main lecture in physiology and became associate professor in 1904. He then went to Germany for a year, studying with Georg von Hüfner in Tübingen, Wilhelm Ostwald in Leipzig, and finally with Emil Fischer in Berlin. There he began work on protein chemistry. He continued this work after his return to Graz, but his main effort was concerned with the chemistry of cholic acids. In this connection he began to elaborate micromethods of elementary analysis. In 1910 he accepted a call to the University of Innsbruck from where he was called back, after three years, to the Medicochemical Institute at Graz. Declining several flattering offers from Berlin and Vienna, he remained faithful to the medical faculty at Graz until he died, December 13, 1930.

Pregl was a forceful personality. He was kindly without being soft, practical without being stolid, a felicitous example of thorough matter-of-factness. The attributes of his life were enduring friendships and lasting, although not hateful, oppositions. When relaxed he could be gay and witty. Unpretentious in his mode of living, open-hearted and direct even in the time of his greatest successes, he was attractive and fascinating. His strongest influence was on his students. His lectures were always interesting and greatly admired because of his clear and precise style, his outstanding skill in experimenting, and his humorous remarks. He was a good friend, adviser, and helper to the academic youth, and he was one of the most active promoters of help during the time of great need after

FRITZ PREGL

the First World War. Through his efforts many a student was enabled to complete his studies.

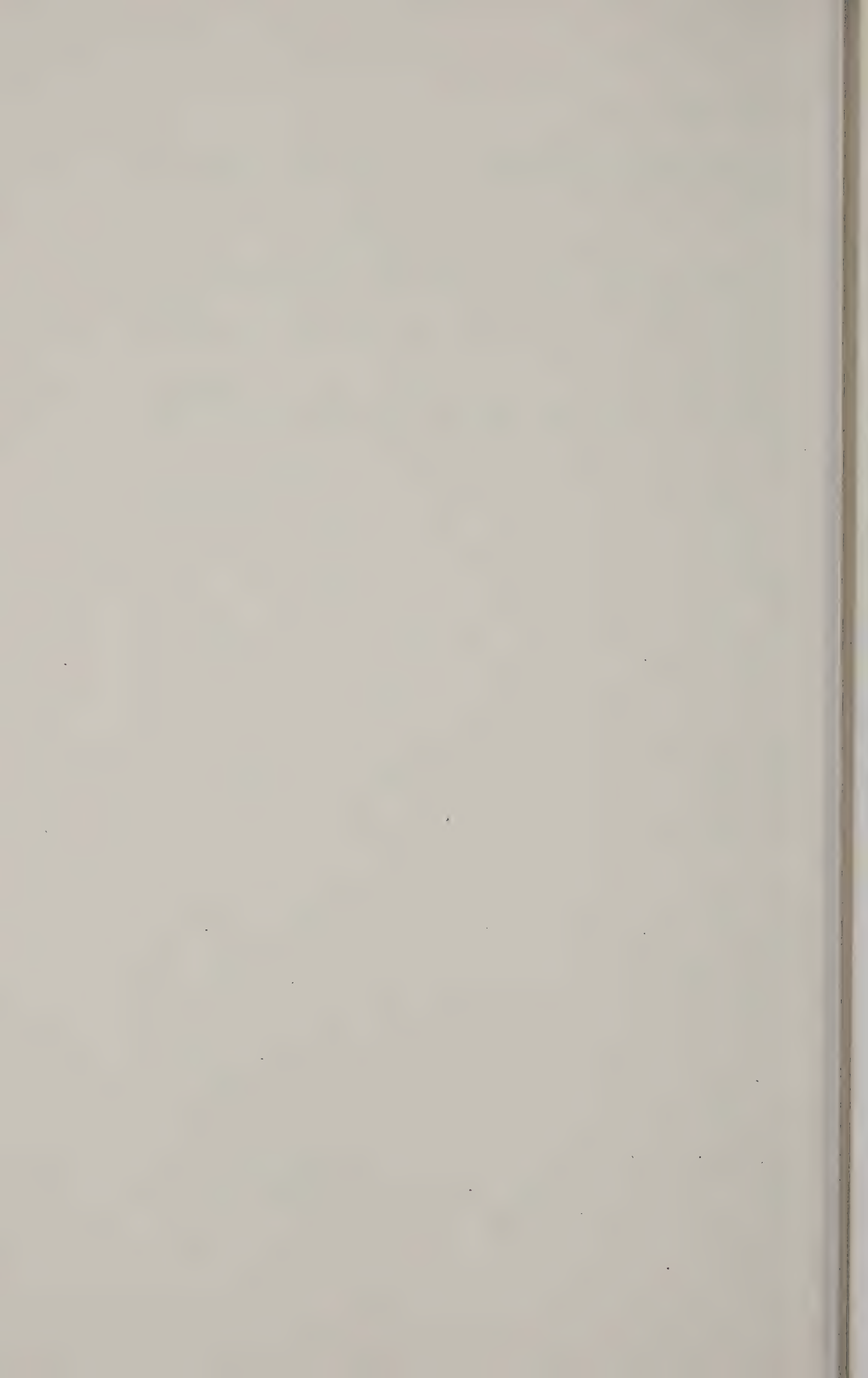
GENERAL REFERENCES

On Friedrich Emich, see: A. A. Benedetti-Pichler, in *Ind. Eng. Chem., Anal. Ed.*, 12, 226 (1940).

On Zdenko Skraup, see: Hugo Schrötter, in *Ber. deut. chem. Ges.*, 43, 3683 (1910).

From: *Mikrochemie ver. Mikrochim. Acta*, XXXV, 123 (1950),
abbreviated. Translated by Eduard Farber.

HANS LIEB



.. 94 ..

Victor Grignard

1871-1935



ON MAY 6, 1871, at 11 o'clock at night, at 51 rue des Carrières in Cherbourg, François-Auguste-Victor Grignard was born to Theophile-Henri Grignard, a chief sailmaker, and his wife, Marie Hebert.

Victor Grignard went to the secondary school of his native city. There he distinguished himself among his co-students. Each year, from 1883 to 1887, his efforts were rewarded by the "prize of excellence." After two years of preparation, he was the winner in the competition for the École Normale Spéciale of Cluny (1889). This school, although scarcely twenty years old, was closed during the reform of the secondary school system in 1891. Grignard acquired the right to one more year of study and was thus transferred to Lyon.

He began to prepare for a degree in mathematics, but he failed, in spite of high intellectual abilities, because his memory was deficient. At that time he fulfilled his obligatory military service without any high ambitions, and thus we shall find him as a corporal at the mobilization in 1914.

After one year in the service he returned to Lyon where he obtained the degree in mathematics and, at the advice of his friend Rousset, also the degree as assistant in the Service de Chimie Générale de la Faculté des Sciences, in 1894. He did this without enthusiasm; from his previous studies he had a very low opinion of chemistry. This science seemed to him unimportant, purely empirical, requiring a memory much better than his. After a short time at the laboratory of Bouveault and Ph. Barbier, those two outstanding representatives of French organic chemistry, what a revelation, what a red face!

In Bouveault, the young lecturer, he found the logician of chemistry, the scholar who was after the crucial experiment to obtain a decisive yes or no answer to a problem. Then, Grignard sought contact with Barbier, and it really was a rude contact with this teacher who was famous for his infinite knowledge. An impetuous, robust researcher, he demanded everything from everyone. This

scientific milieu of fruitful activity quickly inflamed Grignard. He obtained his license *ès Sciences physiques* and succeeded his unfortunate friend Rousset in 1898 as *Chef des Travaux*.

In the same year, Grignard published his first scientific paper, together with Ph. Barbier, on the isopropyl derivative of the ethyl ester of acetylbutyric acid and the stereoisomers of diisopropylhexane dioic acids. After a short publication on a method for obtaining hydrocarbons that have, at the same time, ethylene and acetylene bonds (enines), and on a hydrocarbon with three twin double bonds, Barbier authorized him to continue and generalize a study made by his teacher in 1898. By reacting simultaneously methyl iodide and a ketone, natural methylheptenone, with magnesium, that is replacing zinc by magnesium in the method of Saytzeff, Barbier had obtained the corresponding tertiary alcohol, methylheptenol and thus demonstrated that the use of magnesium permitted to penetrate into the series of the methylketones that is absolutely closed to zinc. This event reached far beyond the narrow confines of synthesis of a new alcohol. However, when Grignard tried to pursue the same principle that should have formed the basis for a general synthetic method, he ran up against the same inconsistent and irregular results that Barbier had encountered. In his calm and slow reasoning Grignard examined the problem more thoroughly. He thought that his chance for success would be improved if he first prepared the organomagnesium compound and only then brought it together with the substance containing the functional group ($-\text{CO}-\text{CH}_3$).

Unfortunately, the method of Löhr for preparing symmetric organomagnesium compounds had to be rejected, especially after the experiences at the laboratory of Lothar Meyer, and even with the modifications by Fleck and Wage. The substances obtained were noncrystallizable, infusible, and insoluble substances of high reactivity, which spontaneously caught fire in contact with dry air or dry carbon dioxide. Therefore, Grignard approached the problem from a new basis.

Frankland and Wanklyn had discovered that by preparing organozinc compounds in the presence of anhydrous ethyl ether, the ether compounds were not inflammable in the air and yet re-

active. Grignard hoped that the same reaction could be obtained with magnesium, which is more electropositive and reactive than zinc. This actually happened, and Grignard thus discovered that, in the presence of dry ether, magnesium reacted with halogenated alkyls at ordinary temperature, and that this reaction, which is practically complete, resulted in ether-soluble organomagnesium compounds.

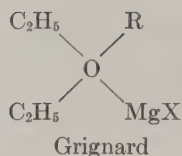
The first publication of these results appeared in the *Comptes rendus* of the Académie des Sciences on May 14, 1900, presented by Moissan. In a few months Grignard explored various directions and established an impressive number of synthetic procedures. This work on mixed organomagnesium compounds and their use in the synthesis of acids, alcohols, and hydrocarbons was presented at the University of Lyon in July, 1901, for the degree of doctor in physical sciences. Moissan suggested to him that he present his thesis in Paris, but Grignard remained faithful to his spiritual cradle and honored it with his first book.

The mixed organomagnesium compounds have such a wide range of reactivities that it was impossible for a single experimenter to develop all the applications. Collaboration was soon begun, and it proved to be of two kinds, voluntary and involuntary. The first proceeded in accord with the inventor and brought him sweet satisfaction. His school was established, a school which, at present (1936) numbers hundreds of experts. The second kind of collaboration was, as usual with all far-reaching discoveries, a contradiction which sometimes makes polemics inevitable and yet was useful for Grignard.

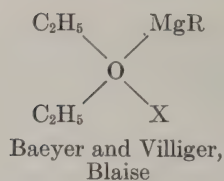
Grignard's scientific life can be divided into three periods: before, during, and after World War I.

From 1901 to 1914 he was mainly occupied with perfecting the initial discovery, interrupted only by social functions. From 1901 on, his collaborator was Tissier, who later became a Senator.

The first discussion on the constitution of organomagnesium compounds occurred between Blaise and Grignard. Both admit the formula $R-Mg-X$, not free, however, but combined with one or several molecules of ether. For the monoether compound, two structures are possible:

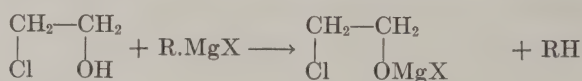


and



(X represents a halogen atom)

It was particularly interesting to study the behavior of halo-hydrines toward organomagnesium compounds. The simplest case is that of the monochlorohydrine of glycol, $\text{CH}_2\text{OH}-\text{CH}_2\text{Cl}$. At low temperature, the reaction involves only the alcoholic group:



The complex thus obtained is capable of reacting with a new molecule of organomagnesium which may well be different from the first:



When R' is the phenyl radical, the result is the phenylethyl alcohol, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, which has the fragrant odor of roses. With this reaction Grignard's discovery first entered industry, in the plant of Descollonges at Lyon.

On November 1, 1905, Grignard started lectures at the Faculté des Sciences in Besançon. The following year he returned to Lyon as Maître des Conférences, so that he was again a member of the department of organic chemistry together with Barbier, and, in addition, had to direct student work at the laboratory. He developed a double activity. Together with Barbier he carried forward a study of the terpenes, and with his students Reif and Abelman he investigated methods of preparing ethylenic alcohols and aldehydes.

Slowly, Grignard climbed the ladder of the academic hierarchy. In 1908 he became associate professor and received the rosette of an Officer of Public Instruction. Not seeing a future for himself at Lyon, he accepted a position at Nancy in November, 1909. A year later, he became professor at Nancy with one of the best equipped provincial laboratories. On the campus of the school, the 150 students of the chemical institute talked about chemistry.

The echoes of the magnificent public garden of the city were full of words like coupling, condensation, grignardization. The followers of Hermes could be easily traced by the strong and characteristic odors with which their clothes were impregnated.

On August 22, 1910, Grignard set up housekeeping. The next year, his worthy companion, Augustine-Marie Boulant, presented him with a son who today is also a chemist.

Wednesday morning, November 13, 1912, at the Faculté des Sciences of Nancy, the rumor of an unprecedented success for the University spread like wildfire. The Nobel Prize in chemistry had been awarded to two scientists of France, Paul Sabatier, dean of science at the University of Toulouse, for his method of catalytic hydrogenation, and Victor Grignard for his discovery of the organo-magnesium compounds. The joy over this great news was immense. At forty-one, Grignard was then the youngest of the Nobel Prize winners.

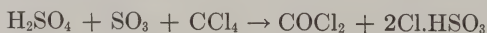
The Congress of the French Association for the Advancement of Science took place at Le Havre, toward the end of July, 1914. A conference was scheduled on "a tunnel under the Channel," a question of burning actuality, when the headlines of the newspapers announced in big capital letters: "To the Austrian ultimatum Serbia replies: No!"

Grignard was mobilized the second of August. The military authorities had known him as a corporal in 1893, for then he was still a corporal in 1914. Professor at the university, Chevalier of the Légion d'honneur, Nobel Prize winner in Chemistry, Grignard became a guard in the Cherbourg region. However, he was soon discovered by the military. Toluene threatened to be in short supply, and Grignard was asked to study the cracking of heavy benzenes. He returned to Nancy where he made a quantitative investigation of the reaction between methylbenzenes and aluminum chloride.

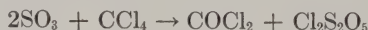
Shortly afterward, on July 10, 1915, practically one year after the mobilization, he was a member of the Chemical War Production Board in Paris where Professor Urbain welcomed his provincial colleague at his laboratory in the Sorbonne. As the director of one of the laboratories for research on war gases, Grignard rendered inestimable services. First he analyzed the

combat gases used by the enemy. More than 2000 analyses were thus carried out on more than 600 samples. Furthermore, numerous investigations were made of our own combat gases, and the control he established in the factories on the basis of laboratory work brought considerable progress in the manufacture of these products. Grignard worked marvels with regard to the many problems in the defense of the country, and he was for World War I what Berthelot had been to the War of 1870.

Of the research done during this period we mention only that part which Grignard was able to publish. He studied the preparation of phosgene by means of oleum and by ordinary sulfuric acid, as well as the utilization of the residues. Sulfuric acid gives twice the yield, with regard to SO_3 , as the reaction of Schützenberger, who uses SO_3 dissolved in pyrosulfuryl chloride. In the first case the reaction is:



whereas in the second:



At 75 to 80°C., ordinary sulfuric acid, with diatomaceous earth as the catalyst, permits obtaining phosgene without having recourse to oleum, although the phosgene is mixed with hydrochloric acid.

The industrial method of producing phosgene with oleum had left several hundred tons of chlorosulfonic acid as a by-product. Grignard utilized it by reaction with ethylene. At temperatures below 20°C. he obtained the chlorosulfate of ethyl, a tear gas.

Yperite, the terrible "mustard gas," ravaged the Allied troops after the fall of 1917. Grignard discovered that a 30 per cent solution of sodium iodide easily replaces the chlorine of yperite by iodine and yields the crystallizable β - β' -diiodide of ethyl sulfide. By studying this reaction, he arrived at a method for detecting one-tenth of a gram of yperite in one cubic meter of air.

On May 30, 1917, Grignard was delegated to represent chemistry in the mission sent over the Atlantic when America joined the Allies. He remained in the United States till the end of January, 1918.

After the armistice, Grignard returned to Nancy and, in November, 1919, he succeeded Barbier in Lyon. We thus approach the third period of his work during which the number of his students grew considerably. Twice he declined offers of a professorship in Paris.

Grignard's profound studies brought us well-rounded knowledge of aldols, ketols, their dehydration products, and the unsaturated alcohols to which they are converted by organomagnesium compounds. These unsaturated alcohols were catalytically hydrogenated, and the splitting of tertiary alcohols did not escape his attention; the dienes from monoethylenic alcohols were closely studied. The chemical constitution of these molecules was frequently established by ozonization. In addition to the normal reactions of the organomagnesium compounds, Grignard observed anomalies like reductions, enolizations of ketones, and condensations. Grignard was not content with observing the phenomenon and exploring its range of application; often he elaborated a theory.

For the saturation of double carbon bonds by hydrogen, two great classic methods appeared normally available, the catalysis by nickel or by platinum. With the method of Sabatier and Senderens, an unsaturated alcohol is completely dehydrated, even at relatively low temperature, and the hydrogenation occurs with the corresponding diene. Grignard avoided the difficulty with great elegance by hydrogenating under reduced pressure. Thus, reducing the concentration on the surface of the catalyst, he avoided the dehydration of the alcohol, at least in part. The remarkable results that he obtained in hydrogenating under reduced pressure seemed contrary to the concepts and theories of the time. Grignard sought new applications for this technique in many directions. Thus he reduced benzaldehyde with a yield of 67 per cent to benzyl alcohol at 150°C. and 100 mm. pressure, and the aldehyde which is not reduced can almost completely be recovered. From benzylidene acetone he obtained increasing yields of the enol by successive reductions of temperature and pressure over a nickel catalyst. The case of the phenols is still more interesting. From several derivatives, and from phenol itself, he produced the tetrahydrophenol or cyclohexanone enol. This, as Grignard wrote,

was a new and clear-cut illustration for Kekulé's benzene formula. Everything occurs as if three double bonds existed in the nucleus; two of them are hydrogenated together, they are those not adjacent to the phenolic function.

Chemical nomenclature was one of the foremost didactic concerns of Grignard. He was an active member of the Commission of Nomenclature of Organic Chemistry in 1912 and, again, in 1921. He collaborated in establishing the rules which this Congress at Liège published, and we find very judicious remarks on these rules in his great opus "Chimie Organique" of which only two volumes appeared before his death, while others have been published posthumously under his name since he had revised them page by page.

This immense work, which he wanted to be perfect, accelerated his end. Full of plans and work he disregarded the illness which undermined him and which, too soon, overpowered him. Grignard died at the age of sixty-four, on December 13, 1935.

GENERAL REFERENCES

- M. S. Kharash, Carl W. Eisendrath, and Otto Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954.
- S. T. Yoffe and A. N. Nesmeyanov, "A Handbook of Magnesium-Organic Compounds," compiled by the Metallo-Organic compounds Laboratory of the Institute of Organic Chemistry of the Academy of Sciences of the U.S.S.R., Pergamon Press, London, (1957).

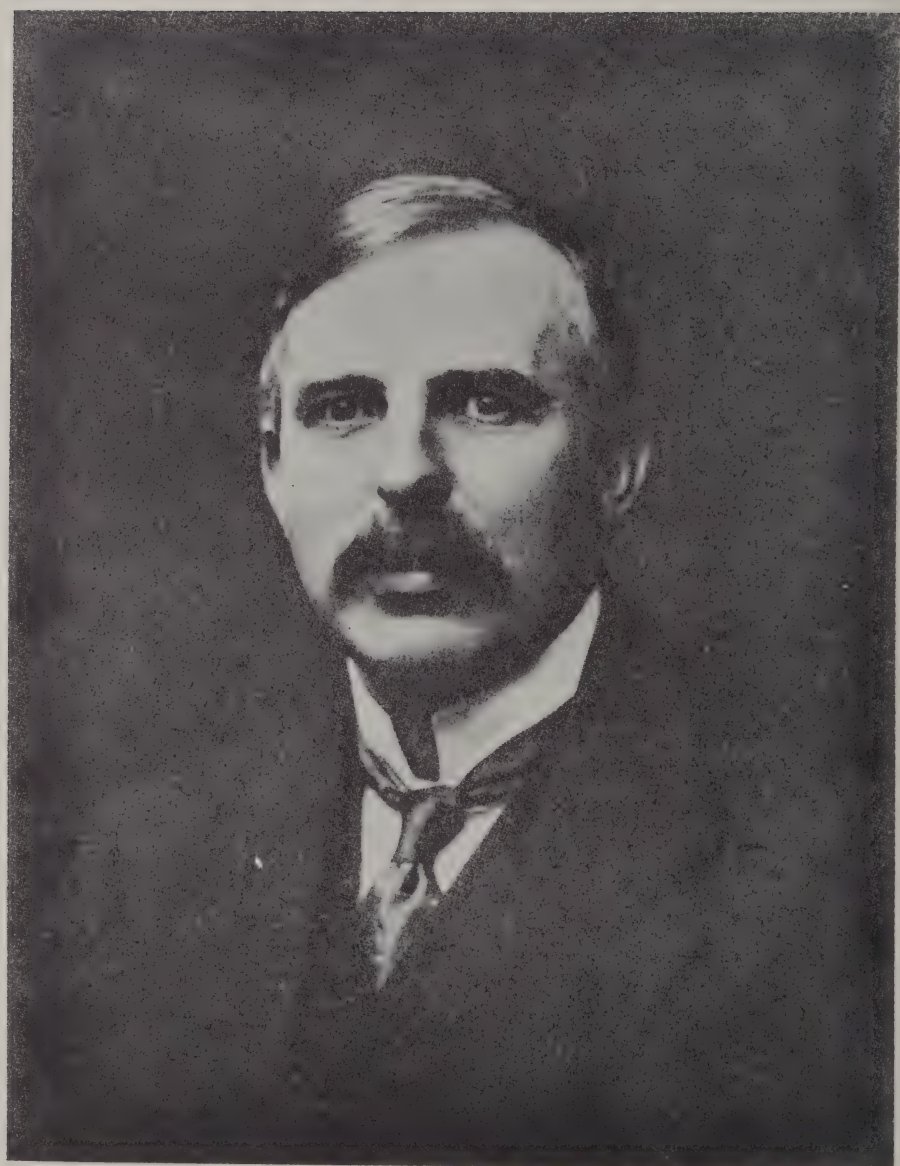
From the biography by Charles Courtot in *Bull. soc. chim. France*, 5^{es.}, 3, 1433 (1936). Translated by Eduard Farber.

CHARLES COURTOT

.. 95 ..

Lord Rutherford

1871-1937



NEW ZEALAND, 1871-1894

IF A NEW country is peopled with a good stock, its future is assured. Such has been the happy fortune of New Zealand, which today justly claims Rutherford as her greatest son. New Zealand was sighted by Tasman and visited by Captain Cook, F.R.S., who stayed long enough to bequeath the flea, the black rat, and the pig to the Maoris. The country received its first white settlers in 1817, but the main colonization followed about 1840—less than a hundred years ago.

Among the early settlers was one of the Rutherfords, for the most part Scots and a virile border folk. His son James, and Martha his wife, another New Zealand settler from Sussex, had four sons and eight daughters. Ernest, the second son and fourth child, was born on August 30, 1871, near Nelson, at Brightwater, and there he went to the State primary school, whence he obtained a scholarship to the Nelson School. About this time his father had moved to Pungarehu, Taranika Province, where he had a flax farm and mill and a rope walk. Rutherford is reported on good authority to have been a normal, happy, unassuming boy, but with unusual powers of concentration—the secret of his success in life. He shot pheasants and wild pigeons, played forward at Rugby football, caught eels and brook trout, nearly drowned himself bathing, took clocks to pieces, made water wheels (like Newton), photographed, loved reading and music; he also won prizes and scholarships for English, History, French, and Latin. He was greatly helped by a good schoolmaster, W. S. Littlejohn, who taught him sound mathematics, and, in a very small class, chemistry and physics. He obtained a scholarship to Christchurch College, Canterbury (part of the University of New Zealand), which at that time (1890) had seven professors and about one hundred and fifty students. Here two men in particular influenced him: Professor A. W. Bickerton, who taught physics and chemistry and was highly original, although "heterodox in all his views and erratic in his methods;" and Professor G. H. H. Cook, whose mathematics was sound and orthodox.

Rutherford's thesis in physics was on "Magnetization of Iron by High-Frequency Discharges," and the necessary experiments were carried out in a cold and draughty den. He showed that high-frequency currents from a small Tesla coil, with a frequency of about 100 million cycles a second, would strongly magnetize iron, contrary to the belief of the day. The explanation was given by the late Lord Rayleigh, who pointed out that with damped oscillations the balance of the total current must necessarily be unidirectional.

Rutherford's second paper was on "Magnetic Viscosity," published 1896 in the *Transactions of the New Zealand Institute*. By this time he was able to send wireless (Hertzian) waves down the 60 feet of the shed, and through walls, detecting them at the other end. He had also, with prophetic insight, read a paper to the Science Society (1891) entitled "The Evolution of the Elements."

For a time he endeavored to impart some of his knowledge to some restless and rather unruly boys of the High School, Christchurch, N.Z.; but—the great opportunity came—the spirit of the Prince Consort kindled New Zealand, and the Commissioners of the great 1851 Exhibition elected the brilliant and promising youth to a scholarship, and he sailed for Cambridge University.

Most of the preceding account is culled from a description of the early years of Rutherford collected by Professor C. C. Farr, F. R. S., Canterbury College, N. Z.

CAMBRIDGE, 1895-1898

On his arrival in England Rutherford joined Trinity College, Cambridge, where later he was elected to a Coutts Trotter Studentship. A wise University regulation had just been made which enabled graduate students of other universities to join Cambridge as research students and obtain a B.A. degree after two years' residence. Sir J. J. Thomson has stated that Rutherford was the very first research student to join him in the Cavendish Laboratory, while J. S. Townsend was a close second.

Rutherford at first continued and developed his work on the magnetic detector already begun in New Zealand and his results were published in *Phil. Trans.*, A, Vol. 198, p. 1 (1897), in a paper which may still be read with great interest. After testing

many types of iron and steel of various lengths and diameters, he finally made a bundle of 20 steel wires (1 cm. long, each 0.007 cm. diameter) and wound them with 80 turns, 2 layers, of fine insulated wire having a total length of 6 inches! The ends of this small solenoid were connected between two straight rods in line, which formed the aerial. The waves came from the oscillator through space and caused a current in the aerial. This current passing round the coil altered the magnetism of the steel and this change was indicated by the deflection of an adjacent small mirror magnetometer. Rutherford used a vibrator or oscillator such as Hertz employed in his classic experiments on wireless waves; the plates were about 16 inches square, but for long ranges he used zinc plates, 6 feet by 3 feet. The sparks between the central knobs were excited either by a Wimshurst machine or a Ruhmkorff coil, and these were equally effective. There was one drawback; the detector had to be remagnetized after the receipt of a signal, a difficulty which Marconi later overcame by the revolution of an endless steel band passing a "washout" magnet. Detection of wireless waves, 6 or 7 meters long, by this method was first made by Rutherford across Jesus Common, Cambridge, over a distance exceeding a quarter of a mile, and later from the top of the Cavendish Laboratory to Park Place, with many brick and stone buildings between oscillator and receiver half a mile apart. Sir Joseph Larmor states that there were also signals sent in this manner from the Cavendish to the Observatory about two miles away. No apology is needed for dwelling at some length on this important pioneer experiment. He received no benefits or specific recognition for his invention, and refused to act as "expert witness" with reference to the discovery.

Rutherford next joined in the investigations on the "Conduction of Electricity through Gases," about which Sir J. J. Thomson published his famous book in 1903—a book which opened great vistas of new regions of physics and was for a number of years almost a bible for physicists. In the index are 25 references to the five or six years of Rutherford's work. Rutherford had ingenious methods for measuring the velocities of the ions produced by Röntgen rays. First he measured the ionization current between two parallel

plates; then he switched off the rays, instantly put on a high potential and thus swept out all the ions of one sign to a plate and measured the charge that this carried with an electrometer. Thus, without knowing either the number or the charge of the ions, it was easy to find the sum of the velocities of the ions in air or in any chosen gas. These added velocities were found to be 10 cm./sec. for hydrogen and 3.2 for air, as for a gradient of 1 volt per centimeter. By another method he measured the velocities of each kind of ion; while his most ingenious scheme was to toss negative ions up and down by an alternating potential until they just reached an upper parallel plate joined to an electrometer. Rutherford was the first to measure the coefficient of the rate of recombination of ions. All of which justified his remark that "Ions are jolly little beggars, you can almost see them!"

In the meantime great events were happening in France. Henri Becquerel had shown that uranium was radioactive (1896); Marie Curie had discovered polonium; Pierre and Marie Curie had found radium (1898); the next year Debierne produced actinium. All of these bodies had new, strange, complex properties. At Cambridge, Rutherford, now highly trained, began to study the radiations from uranium, and when he was appointed Macdonald Research Professor of Physics at McGill University, Montreal, to succeed H. L. Callendar, he carried this work with him with far-reaching results.

MCGILL UNIVERSITY, 1898-1907

At Montreal, Rutherford continued his work on the radiations from uranium and found that there were two types, which he named alpha and beta rays, whose absorptions by aluminum foil were in the ratio of a hundred to one. He noted in the case of thorium a yet more penetrating type, but the name gamma rays was given later by Villard. About the same time R. B. Owens began work at McGill on the radiations from thorium compounds and found some perplexing new properties, for a draft of air would reduce his electroscope readings to a third of their value in still air, and "something" would pass through paper which could not get through quite thin layers of mica or metal foil. Rutherford

examined this problem in a systematic way and found that there was an "emanation," quite different from ionized air, for it would pass through cotton wool or red-hot metal tubes, losing half its strength about every minute. Moreover, this substance would render other bodies radioactive, so that there were now four things to think about in the case of thorium—alpha rays, beta rays, emanation, and "induced" or "excited" activity, later known as "active deposit." It was well remarked at the time that "it will be seen that radioactivity is a very complicated phenomenon." This discovery of thorium emanation (thoron) was an important advance, followed by Dorn (1900) finding radium emanation with a half-value period of about four days. This, too, gave rise to "induced radioactivity" as Mme. Curie found.

Sir William Crookes ingeniously extracted by chemical methods uranium X—a highly radioactive material relatively small in quantity—from uranium nitrate, which thereby became weaker; but the new substance grew weak (half-value period one month) and the original uranium recovered at the same kind of rate. Rutherford and Soddy somewhat similarly extracted thorium X from thorium and watched the former, at first strongly radioactive, weaken day by day, following an exponential law, while the original thorium recovered its radioactivity in a strictly complementary manner. In this case the period of half-value, regardless of age, was four days.

With this somewhat scanty but definite evidence, (Rutherford had also found an exponential law of decay for thorium emanation and active deposit) Rutherford and Soddy (1902) boldly set forth the theory of radioactive change. They claimed that radioactivity was an *atomic* property, independent of physical surroundings or chemical composition, and it was stated that "the normal or constant radioactivity possessed by thorium is an equilibrium value, where the rate of increase of radioactivity due to the production of fresh active material is balanced by the rate of decay of radioactivity of that already formed" (*Phil. Mag.*, vol. 6, 3, p. 569, 1902).

The importance of the word "material" may be emphasized. A year later came a clearer statement; writing of a single radioactive

substance, the principle is laid down: "The rate of the change of the system at any time is always proportional to the amount remaining unchanged." Here speaks the perfect actuary dealing with the mortality tables of disintegrating atoms. He continues: "The proportional amount of radioactive matter that changes in unit time is a constant." This constant for any given material is here called for the first time the "radioactive constant." It is of course simply and closely connected with the half-value period, and its reciprocal is the average life of the atoms.

After these general principles had thus been laid down there was little stumbling in their application. Rutherford, with consummate skill, mastered the radium family, viz., radium, radon, radium A-F, all in strictly linear descent. He identified radium F with Mme. Curie's polonium, for the two had the same period of decay to half-value. He also postulated the existence of two "rayless" changes RaB and RaD, which are now known to project beta particles, but at the time they were mere go-betweens, devoid of all physical properties, but none the less "real." He presented the whole fabric complete with theory to the Royal Society in his Bakerian Lecture. (*Phil. Trans. A*, vol. 204, pp. 169-219, 1904.)

In 1908 Boltwood was praising the then recent papers of Rutherford and Geiger. "These are quite up to the top notch of your own standard and I think the best since the Bakerian Lecture period, which in my opinion can never be beaten. That Bakerian Lecture is going down through history as *the classic*, and every time that I turn to it I am comforted with the thought that I possess a copy."

Rutherford was elected Fellow (1903) and awarded the Rumford Medal (1905). Before this, however, he had revisited his home in New Zealand and married (1900) Mary G. Newton, only daughter of Arthur and Mary de Renzy Newton, Christchurch, N.Z.

The great benefactor of McGill, Sir William Macdonald, presented to the laboratory a liquid air machine and a hundred milligrams of Ra Br₂; with these Rutherford quickly showed that radium emanation was a gas which would condense in a spiral tube immersed in liquid air at a temperature of about 153°C. At

ordinary temperatures, the emanation behaved like a gas and diffused at a rate suggestive of high molecular weight. Moreover, it disintegrated at a rate independent of the volume it occupied, so that atoms were not disintegrated by the radiation from adjacent atoms.

Curie and Laborde had found that a gram of radium would produce heat continuously at the constant rate of about 100 calories an hour. Rutherford and Barnes confirmed this and found how the heat arose with reference to the different types of radiation, also with respect to the various members of the radium family. Rutherford made a calculation relating to this high output of energy and added "there is no reason to suppose that this enormous store of energy is possessed by radioelements alone" (*Phil. Mag.*, vol. 6, 5, p. 587, 1903). Indeed, were it possible to collect a pound of radium emanation the rate of output of its radiant energy would at first be equivalent to 10,000 or 100,000 horsepower. Rutherford and Soddy had stated that "on the disintegration hypothesis this energy is derived from the latent energy in the radium atoms and is released in the successive stages of their disintegration."

In 1903 Rutherford published important results on the nature and measured properties of alpha rays from radium, which he passed between parallel plates and deflected with magnetic and electrostatic fields. He found the ratio of charge to mass of an alpha particle to be about 6000, which suggested a helium atom of mass 4 and with charge $+2e$, as was finally proved. He found the velocity of the alpha particle to be about 2.5×10^9 cm./sec.—rather too large a value. But these early results gave a clear enough picture of the nature of this radiation. In 1905, while still at McGill, Rutherford had fired alpha particles into a testing chamber and determined the total charge carried per second. Knowing the double charge that each carried, he was able to state that the number of alpha particles issuing from a gram of radium every second was about 6×10^{10} , and of beta particles 7.3×10^{10} , while the half-value period of radium was estimated at 1850 years. (*Phil. Mag.*, vol. 6, 10, p. 193, 1905.) These figures were based on an erroneous radium standard and on too low a value of the

electronic charge, yet for first measurements they were astonishingly, perhaps luckily, good.

MANCHESTER, 1907-1919

In 1907 Rutherford accepted the Langworthy Chair of Physics in the University of Manchester. His predecessor in the chair, Professor Arthur Schuster, was largely responsible for the invitation which was sent from Manchester to Rutherford. The laboratories to which he came were fairly new (they had been opened in 1900), and Schuster had devoted much care to their design and equipment. Two subdepartments, electrotechnics (later separated into an independent department under Professor R. Beattie) and electrochemistry, were housed in the physics building and under the control of the Langworthy Professor. The laboratories as a whole were well equipped for electrical work, and there was an efficient liquid air machine. In other words, the laboratories were so equipped that Rutherford could continue, with a minimum of delay, the work he had begun in Canada. He was not hampered by excessive teaching or administrative duties, he had a capable teaching staff to assist him, and he found in Mr. William Kay a young, energetic, and exceptionally capable laboratory steward. The department ran smoothly and Rutherford was able to throw a large part of his amazing energy into the development of a school of radioactive research. In a short time he attracted so many research workers from all parts of the world that the laboratory became seriously overcrowded. Conditions were much relieved by the building, some four or five years later, of additional research rooms and the removal of the subdepartment of electrotechnics to a separate block.

Two circumstances facilitated the beginning of work in Manchester. He found there Schuster's young assistant, H. Geiger, who became an admirable second in furthering the development of a research school; and in 1908 the Akademie der Wissenschaften of Vienna lent him 250 milligrams of radium, a very considerable amount of radium in those days. The radium preparation was of low concentration and so bulky that it was unsuitable for most experiments. Rutherford therefore developed a new way of using

radium—the use of radium in solution as a source for its emanation, which could be pumped off when required. The apparatus for this purpose and the method of purifying the emanation were worked out with the aid of Royds (*Phil. Mag.*, November, 1908). This was a significant advance in technique, for it made possible a regular supply of radium emanation and an active deposit for the many experiments in progress in the laboratory.

Rutherford's work at McGill had firmly established the transformation theory propounded by himself and Soddy, and the general scheme of the radioactive families was sufficiently clear, at least in outline, by 1907. At the time of his arrival in Manchester he was more keenly interested in the radiations from the radioactive substances, and especially in the x-rays, than in the substances themselves.

One of his earliest major contributions in Manchester was the beautiful work with Geiger (*Proc. Roy. Soc., A*, vol. 81, p. 141, 1908), in which the number of α -particles emitted per second per gram of radium was accurately and directly measured for the first time. It is difficult now to realize the many difficulties which had to be overcome before they were able to detect a single α -particle by means of its electrical effect. It was a technical feat of a high order, all the more impressive for having been accomplished with the simplest apparatus and in a very short time. The result of this measurement was of the utmost value in general atomic theory, as well as in radioactivity. When combined with the measurement of the total charge carried by a stream of α -particles (Rutherford and Geiger, *Proc. Roy. Soc., A*, vol. 81, p. 162, 1908) this result showed clearly that the normal α -particle was doubly charged, and gave a value for the unit of charge which was at least as reliable as any available at the time.

Rutherford's earlier work had convinced him (and most other physicists) that the α -particles were doubly charged helium atoms. Although the new work with Geiger strongly supported this view, he evidently felt the need of a direct identification. This followed in the experiment with Royds (*Phil. Mag.*, vol. 17, p. 281, 1909). They succeeded in preparing glass tubes with walls so thin that α -particles could pass through and yet so strong as to withstand

atmospheric pressure. Such an " α -ray tube" was filled with radon and the emitted α -particles were allowed to emerge into a previously evacuated space. After a few days, an electrical discharge was passed through this space and the characteristic spectrum of helium appeared. This experiment created great interest on account of its simple directness and beauty.

It was, however, the experiments on the scattering of α -particles which led to Rutherford's greatest and most fruitful contribution to atomic theory. In the experiments on the counting of the particles it had been noticed that traces of residual gas in the long tube down which the α -particles passed had an influence on the counts. This effect was ascribed to a small scattering of the α -particles, which was investigated later by Geiger (*Proc. Roy. Soc., A*, vol. 81, p. 174, 1908; vol. 83, p. 492, 1910). Then came the surprising observation by Geiger and Marsden (*Proc. Roy. Soc., A*, vol. 82, p. 495, 1909) that an α -particle sometimes experienced an exceptionally violent deflection, seldom, it is true, but far too often to be explained on the basis of the previous measurements of the scattering. Rutherford must have pondered deeply on this curious effect. Professor Geiger writes: "One day (in 1911) Rutherford, obviously in the best of spirits, came into my room and told me that he knew now what the atom looked like and how to explain the large deflections of the α -particle. On the very same day I began an experiment to test the relation expected by Rutherford between the number of scattered particles and the angle of scattering." The genius of Rutherford had seized upon an apparently unimportant detail and transformed it into a clue to the problem of the inner structure of the atom. The nuclear theory of atomic structure was published in a surprisingly complete form in 1911 (*Phil. Mag.*, vol. 21, p. 669, 1911). Supported at first by the preliminary experiments of Geiger on the variation of scattering with angle, it was in the next few months confirmed in its minutest details by a beautiful series of accurate quantitative tests. It would be difficult to exaggerate the influence of the nuclear theory of atomic structure on the whole range of the exact natural sciences, and the theory will surely rank as the greatest of all Rutherford's contributions to physics.

Soon after the publication of the nuclear theory came two researches which are now classic. The first of these was Bohr's earliest contribution to atomic physics, in which he applied quantum-mechanical principles to the Rutherford model of the atom. Bohr had spent a few months in Manchester in the early summer of 1912, where he began to think about the rôle played by the quantum of action for the stability of the Rutherford atom. Only after his return to Denmark, however, did he produce his great paper on the constitution of the atom, in which he showed how the fundamental rules of the spectra of the elements could be explained in a very simple way. The second piece of work was Moseley's brilliant investigation of the x-ray spectra of the elements, in which he demonstrated the function of the nuclear charge in determining x-ray spectra and established the importance of the concept of atomic number. These two researches, which are among the most illustrious of a long line depending upon Rutherford's nuclear atom, undoubtedly owed much to his personal inspiration.

Not long afterward, the Manchester research school was almost completely dispersed as a result of the outbreak of war. Much of Rutherford's time was taken up by war work, as well as by the difficulties of running his department with a heavily depleted staff. In 1919, however, he was able to publish the results of yet another epoch-making research, again made with α -particles. In four papers published in the *Philosophical Magazine*, Vol. 37, he proved conclusively that the long range particles earlier shown by Marsden to be produced when α -particles were fired into hydrogen were in fact fast hydrogen nuclei, and he showed that identical particles were produced by the collisions of α -particles with nitrogen. The explanation—that these protons were the result of the disruption, or “artificial disintegration,” of the normally stable nitrogen nucleus—was so revolutionary, and so pregnant with far-reaching implications, that it clearly needed to be supported by very complete experimental evidence. Rutherford obtained the necessary support by an admirably designed series of control experiments. He did the whole of the experimental work, with Kay's assistance in taking observations of scintillations. The further

development of this work, and its extension to other nuclei, belongs to the Cambridge period.

WAR WORK, 1914-1918

World War I produced marked changes in Rutherford's laboratory in Manchester. The "family" of research workers dispersed—joining various branches of the fighting forces.

In July, 1915, the Admiralty Board of Invention and Research (B.I.R.) was organized under the presidency of Lord Fisher. Rutherford was on the Panel of the Board and on the Sub-Committee dealing with submarine detection and location, besides other important matters. At that time, enemy submarines were just becoming troublesome; later they became a menace.

It might have been supposed that a man like Rutherford could not "switch over" from atoms to submarines. No doubt such a change required a great effort on his part, but he was equal to it and tackled the problem with his customary energy. The large research laboratory on the ground level was transformed into an acoustics laboratory with a large tank for studying underwater acoustics, about which little was known. His early work in this laboratory with Broca tubes, diaphragms, microphones, and various underwater senders and receivers demanded tests under service conditions. A research station was started at Hawkerai, Aberdour, in November, 1915. Rutherford supplied a constant stream of apparatus and ideas to be tried out on ships and submarines at Aberdour.

CAMBRIDGE, 1919-1937

When Rutherford went to Cambridge in the summer of 1919 he took with him a great deal of apparatus from Manchester, including the Vienna radium, so that he was ready to start work immediately. He continued his investigation of the effects accompanying the passage of α -particles through nitrogen and oxygen, recorded in the series of papers in the *Philosophical Magazine* of 1919. The results of these experiments were given in his second Bakerian Lecture of 1920, "The Nuclear Constitution of Atoms." He gave further and conclusive proof that the long range particles

from nitrogen were swift protons, by measuring their deflection in a magnetic field. This was the first great step in the deliberate transmutation of matter. He also discussed the nature of the "short range atoms" observed in nitrogen and oxygen, and concluded that they were a new kind of particle of mass 3 and charge 2, that is, an isotope of helium, liberated in the disintegration of nitrogen and oxygen. This conclusion proved to be wrong, for these "short range atoms" were found later to be "long range α -particles" emitted by the source of radium C. This is one of the very few instances in which Rutherford made a wrong deduction from his experiments. The apparent occurrence of this new particle—part of the structure of the nitrogen and oxygen nuclei—led him to consider generally the constitution of atomic nuclei. Using as the ultimate constituents the hydrogen nucleus and the electron, he suggested that simple combinations of these might exist which had not yet been discovered. It may be of interest to quote his own prophetic words forecasting deuterium and neutron:

. . . it seems very likely that one electron can also bind two H nuclei and possibly also one H nucleus. In the one case, this entails the possible existence of an atom of mass nearly 2 carrying one charge, which is to be regarded as an isotope of hydrogen. In the other case, it involves the idea of the possible existence of an atom of mass 1 which has zero nuclear charge. Such an atomic structure seems by no means impossible. On present views, the neutral hydrogen atom is regarded as a nucleus of unit charge with an electron attached at a distance, and the spectrum of hydrogen is ascribed to the movements of this distant electron. Under some conditions, however, it may be possible for an electron to combine much more closely with the H nucleus, forming a kind of neutral doublet. Such an atom would have very novel properties. Its external field would be practically zero, except very close to the nucleus, and in consequence it should be able to move freely through matter. Its presence would probably be difficult to detect by the spectroscope, and it may be impossible to contain it in a sealed vessel. On the other hand, it should enter readily the structure of atoms, and may either unite with the nucleus or be disintegrated by its intense field, resulting possibly in the escape of a charged H atom or an electron or both.

And further:

The existence of such atoms seems almost necessary to explain the building up of the nuclei of heavy elements; for unless we suppose the production of charged particles of very high velocities it is difficult to see how any positively charged particle can reach the nucleus of a heavy atom against its intense repulsive field.

The idea that there might exist small particles with no electric charge had, of course, been suggested many times before, but none of these suggestions so closely forecast the properties of the neutron we now know. Rutherford thought that these neutral particles might be formed in the electric discharge through hydrogen. Several experiments were made to test this idea, but they gave, of course, negative results. Rutherford never abandoned the idea that the neutron might exist, and in later years both he and Chadwick made unsuccessful attempts to detect this particle (cf. Rutherford and Chadwick, *Proc. Camb. Phil. Soc.*, vol. 25, p. 190, 1929).

After going over the ground of his previous work in this way, Rutherford, with Chadwick, extended the work on disintegration by the impact of α -particles on other elements. Improvements in the technique of scintillation counting made observations much easier and more reliable, and it was rapidly shown that many of the lighter elements could be disintegrated, with the emission of long range particles (Rutherford and Chadwick, *Phil. Mag.*, vol 42, p. 809, 1921). In a later paper it was shown with reasonable certainty that the long range particles were in all cases swiftly moving protons. In subsequent papers the observations were further extended and it was shown that nearly all the light elements, up to argon, were disintegrated in this way. The mechanism of the disintegration process was not at first clear. It was gradually realized that a kind of synthesis of the atomic nucleus probably took place, in which the α -particle was captured and incorporated into the nuclear structure, and a proton emitted. This capture of the α -particle was later shown very clearly and decisively in the beautiful experiments of Blackett in which he observed and photo-

graphed disintegrations of nitrogen in the expansion chamber. The general view (*cf.* Rutherford and Chadwick, *Proc. Phys. Soc.*, vol. 36, p. 417, 1924) was that, while the ordinary Coulomb force must hold outside the nucleus, there must be attractive forces inside in order to hold the particles together. There must then be a critical surface around the nucleus at which the force is zero or the potential a maximum. In order to promote a disintegration, the α -particle had to penetrate within this critical surface. There should thus be a minimum velocity which the α -particle must have to produce a disintegration and the proton must escape from the nucleus also with a certain minimum velocity. The experiments gave general support to this view of the disintegration process. Estimates of the critical potential (which we should now call the height of the potential barrier) agreed reasonably well and the probability of disintegration also fitted in with this view. It is not without point to remark how well this general picture corresponds to our present ideas.

Pursuing this conception, Rutherford attempted to obtain further information about the potential barriers around atomic nuclei by investigating the scattering of the α -particles (Rutherford and Chadwick, *Phil. Mag.*, vol. 50, p. 799, 1925). He found that the scattering by light elements departed in a striking way from the normal scattering calculated on Coulomb forces. While the deviations occurred in about the expected region it was not possible to give a satisfactory explanation of the results. A still more striking result was obtained from the examination of the scattering by uranium. As uranium emits α -particles of 2.7-cm. range it was expected that α -particles of radium C', of much greater energy, would be able to penetrate with ease into the uranium nucleus; such penetration would be revealed by strong divergences from normal scattering. No such divergences were observed; the forces experienced by the α -particle were the ordinary Coulomb forces. The radioactive data gave a radius of at least 7×10^{-12} cm. for the uranium nucleus, the scattering experiments said it was less than 3×10^{-12} cm. To escape from this dilemma, the suggestion was made that the outer parts of a nucleus were composed of neutral satellites. Rutherford himself developed this point of view

later in great detail (*Phil. Mag.*, vol. 4, p. 580, 1927) in an interesting way, but without real success. The difficulty was too deep-seated. Classical mechanics failed to describe these events. The explanation was given by Gurney and Condon, and by Gamow, a year or so later, when they pointed out that the wave mechanics allowed the α -particle to escape from a nucleus through the potential barrier, and did not force it, as did the classic mechanics, to climb over the top.

The transmutation of elements, so long and so often sought and at last by him achieved, the crowning triumph of his life's work, held for Rutherford a profound fascination. Perhaps he dimly foresaw the boundless possibilities, not yet conceivable. He was able to convey some of this quiet satisfaction and enthusiasm in that last book of his, "The Newer Alchemy," which has given so much pleasure to many readers of varied types of thought.

This work on disintegration by high-speed ions was pushed on with great vigor, and he and Oliphant, with various collaborators, obtained a great many interesting and important results. The energy relations in some of the processes led Rutherford and Oliphant to the conclusion that the values accepted for the atomic masses of the light elements were inconsistent. They deduced, from their experiments, a new set of atomic masses and this work acted as a fresh stimulus to measurements by Aston using the mass spectrograph.

During his years in Cambridge, Rutherford's influence spread far and wide. As his insight and sound judgment became more widely appreciated, the claims on his time and services grew. He was consulted on awards and appointments by societies, universities and government departments. There were his annual lectures at the Royal Institution; of which he was professor of physics, where he demonstrated admirably his latest discoveries. He was in demand for lectures, meetings, and addresses both at home and abroad.

HONORS

In 1893 Rutherford obtained his M.A. degree with honors in mathematics and physics from the University of New Zealand, and

LORD RUTHERFORD

in 1894 he was elected to an 1851 Exhibition Scholarship. He became fellow of the Royal Society in 1902, and three years later was awarded the Rumford Medal. He was Nobel Laureate for chemistry, 1908, and received the honor of knighthood in 1914. He was elected fellow of Trinity College, Cambridge (1919), and awarded the Copley Medal of the Royal Society (1922). He was president of the British Association for the Advancement of Science (1922). He received the great distinction of the Order of Merit (1925). He was president of the Royal Society (1925–1930), and he was professor of natural philosophy at the Royal Institution. He was president of the Institute of Physics and an 1851 Exhibition Commissioner. He received the Barnard Medal from Columbia University, the Franklin Medal (1924) from the Franklin Institute, Philadelphia; the Albert Medal (1928) from the Royal Society of Arts; the Faraday Medal (1930) from the Institute of Electrical Engineers; and, as early as 1908, the Bressa Prize (£384) from the Academy of Sciences at Turin—his first substantial recognition. He received honorary degrees from about twenty universities scattered over the world, and he was an honorary member of numerous societies and academies, as recorded in the Year Book of the Royal Society.

In 1931 he was created Baron Rutherford of Nelson and took his seat in the House of Lords.

In 1937 he was elected president of the twenty-fifth (silver jubilee) meeting of the Indian Science Congress joined by nearly a hundred representatives of the British Association for the Advancement of Science. His presidential address, prepared about two months before his untimely death, was read (January, 1938) by his successor, Sir James Jeans, who paid a noble tribute to this friend he so admired and respected. He said:

In truth most of his investigations were key investigations, each brilliant in its simplicity of conception and far-reaching in its consequences . . . In his flair for the right line of approach to a problem, as well as in the simple directness of his methods of attack, he often reminds us of Faraday, but he had two great advantages which Faraday did not possess—first, exuberant bodily health and energy,

and second, the opportunity and capacity to direct a band of enthusiastic co-workers. Great though Faraday's output of work was, it seems to me that to match Rutherford's work in quantity as well as in quality, we must go back to Newton.

Voltaire once said that Newton was more fortunate than any other scientist could ever be, since it could fall to only one man to discover the laws which govern the universe. Had he lived in a later age, he might have said something similar of Rutherford and the realm of the infinitely small; for Rutherford was the Newton of atomic physics. In some respects he was more fortunate than Newton; there was nothing in Rutherford's life to compare with the years which Newton spent in a vain search for the philosopher's stone, or with Newton's output of misleading optical theories, or with his bitter quarrels with his contemporaries. Rutherford was ever the happy warrior—happy in his work, happy in its outcome, and happy in its human contacts.

Like Faraday, Rutherford lived to be a centre of universal affection as well as esteem . . . He had, of course, a volcanic energy and an intense enthusiasm—his most obvious characteristic—and an immense capacity for work. A "clever" man with these advantages can produce notable work, but he would not be a Rutherford. Rutherford had no cleverness—just greatness.

He could not fail to be aware of this, but, like his honors, it left him quite unspoiled. On the occasion of one of his discoveries, the writer said to him: "You are a lucky man, Rutherford, always on the crest of the wave!" To which he laughingly replied, "Well! I made the wave, didn't I?" and added soberly, "At least to some extent." Truly his wave went with him wherever he went, a fine wave, lit by the sunbeams, for he had the three precious gifts of the poet—deep insight, powerful imagination, and a profound love of truth. And so it came to pass that he was "always a charming blend of boy, man, and genius."

There came a short, sharp illness, an operation, and in spite of every care he died on October 19, 1937.

Six days later his remains were laid to rest in the Abbey near the graves of Newton, Kelvin, Darwin, and Sir John Herschel. He had been created Baron Rutherford of Nelson in 1931, but he will always be Rutherford. The words of the Sub-Dean of West-

LORD RUTHERFORD

minster remain with us: "We thank thee for the life and works of Ernest our brother."

GENERAL REFERENCES

A. S. Eve, "Rutherford 1871-1937, being the life and letters of the Rt. Hon. Lord Rutherford," Macmillan, New York, 1939.

"Rutherford by those who knew him; being the collections of the first five Rutherford-lectures of the Physical Society," The Physical Society, London, 1954.

Selections from: *Obituary Notices of Fellows of the Royal Society*,
No. 6, 2, 395 (January 1938).

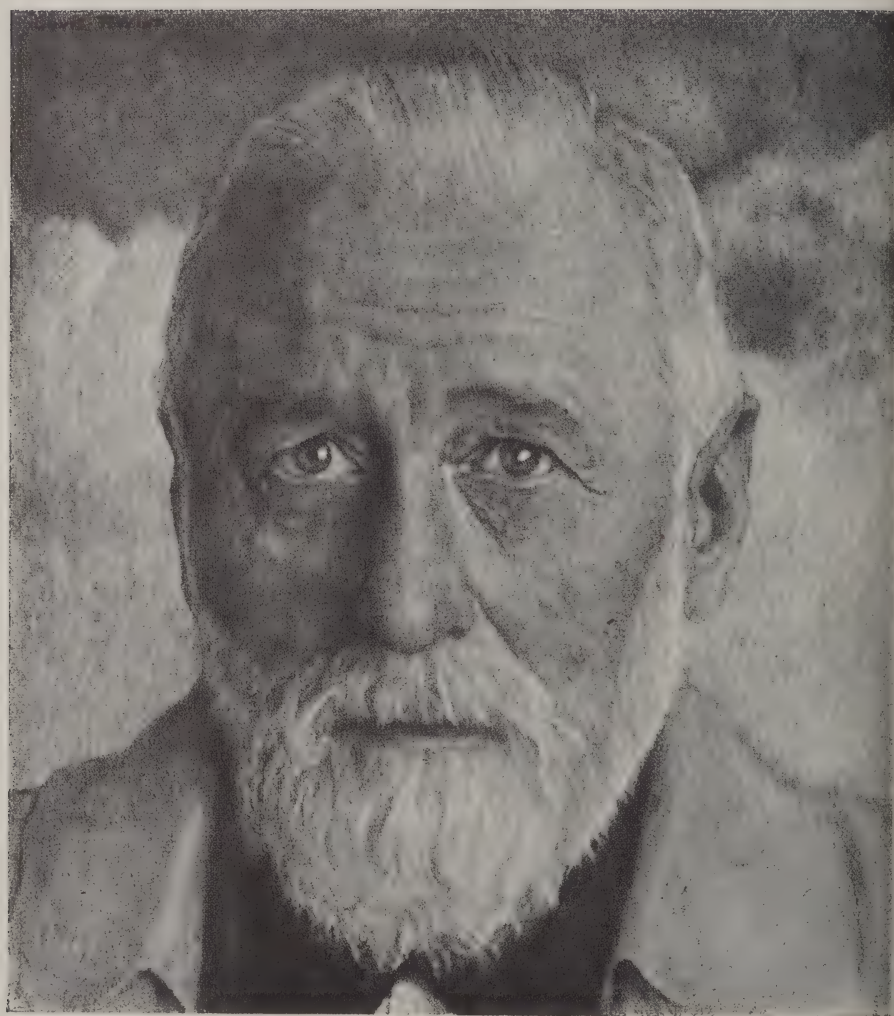
A. S. EVE

J. CHADWICK

.. 96 ..

Richard Willstätter

1872-1942



LIKE Wilhelm Ostwald, Richard Willstätter left us an autobiography, with the difference, however, that its publication occurred after his death, through the devotion of his former assistant Arthur Stoll.¹ Again like Ostwald, Willstätter resigned from his professorship, the former at the age of fifty-three, the other at fifty-two, and both for reasons connected with religion. There the likeness ends; Willstätter resigned in protest against anti-Semitism among the faculty at his university. In fact, the differences between these two great men are more pronounced than the similarities. Willstätter was not a prolific writer; he collected his research papers in only three books: on chlorophyll, on the assimilation of carbon dioxide by the green leaf, and on enzymes. This reveals another difference from the outstanding physicochemist, Ostwald. They also differed in their outlook on philosophy and in their relationship to art. Willstätter had little inclination toward music: "I experienced more strongly through the eye than by ear."² Ostwald was, in a creative sense, self-centered; in his autobiography he describes mostly his own life story, seen as the result of certain generally valid laws which it exemplified. Willstätter in his autobiography relates much more about his friends and colleagues. He says many penetrating and, often, humorous things about them. A deep interest in the history of their science was shared by both, but Ostwald expressed it in historical studies, while Willstätter confined his activities in this field to the search and acknowledgment of predecessors in his special research work. Both disliked to search the literature before they started work on a new idea, but Willstätter expressed the reason differently:

What I was not always inclined to do was to examine the literature of the adjacent sciences, physics, botany, physiology, *before* the experiment. It is too difficult, it is often enough repelling, to distinguish the dim path between right and wrong before one's own experimenting. It is different when clear experimental results have

been achieved, then you can always find predecessors and previous accomplishments.³

Richard Willstätter was born on August 13, 1872, in Karlsruhe, as the second son of Max Willstätter, a textile merchant, and his wife Sophie, née Ulmann. Both parental families had lived in southern Germany for many centuries. The great-grandfather of Richard's grandfather, a rabbi, came to Karlsruhe in 1720 from the small Alsatian town of Willstätt. Two great-uncles also were rabbis. The father was not too successful in his business; he went to New York for several years, so that the responsibility for the education of the boys rested largely on the mother's shoulders.

During his school years, at the age of twelve, Richard "was decidedly for chemistry and the natural sciences in general."⁴ Thus, when he entered the Technische Hochschule at Munich in 1890, he gave much time to botany in addition to chemistry. Medicine and physiology also attracted him, but his mother opposed them as a preparation for a profession.

In Munich, Richard assisted Alfred Einhorn (1857-1917) in his work on cocaine, the main alkaloid of the coca leaves, which had great medical importance. His doctor's thesis of 1895 was in this field, and he concluded the work four years later with the proof that cocaine contained a seven-membered carbon atom ring.

The new scientific result had interesting practical consequences. The new products synthesized by Willstätter were of great medical value as narcotics. The house of Merck in Darmstadt had offered Willstätter an agreement for the industrial development of these findings. "I did not work with an industrial application in mind. However, the solution to an industrial problem, or some new technical method, frequently happened without being intended or expected."⁵

Sometimes, however, the application was clearly intended and predicted by Willstätter. When a derivative of trichloroethanol proved to be a mild sedative, he directed work toward the corresponding substances containing bromine instead of chlorine. Thus, Voluntal and Avertin came to be added to the chemical pain relievers and anesthetics. They were by-products of his later work

on fermentations and enzymes. The name Voluntal was coined by Carl Duisberg (1861–1935), head of the Farbenfabriken vormals Fr. Bayer and Co., who told Willstätter: "We are going to treat you like Emil Fischer."⁶ This meant a very substantial support of Willstätter's work, until the dramatic change in his life.

After his graduation Willstätter had become a private assistant to Adolf von Baeyer, a cooperation which developed into personal friendship. Willstätter remained in Munich till 1905 as Privatdozent (1896), associate professor (1902) and head of the department of organic chemistry. In 1903, he married the daughter of professor Emanuel Leser. She died five years later. A son and a daughter were born to them.

In 1905, Willstätter accepted a call to the Technische Hochschule in Zürich and occupied the chair in chemistry till 1912. These were particularly fruitful years, devoted mostly to substances of the quinone group and to the chemistry of chlorophyll.

The study of the quinone group was related to the work at Munich. A continuation of the cocaine investigations led to an intriguing new substance, obtained from an alkaloid present in the root bark of the pomegranate tree. This new substance resembled benzene in structure insofar as its eight carbon atoms formed a ring and were alternately connected by single and double bonds. It was, therefore, designated as cyclooctatetraene. In spite of the structural analogy to benzene, it behaved like an unsaturated aliphatic compound.

Through new methods of extraction, solvent application, and judicious use of acid and alkali as specific splitting agents, he made important contributions to chlorophyll chemistry. "My third paper on chlorophyll was the high point on my scientific way."^{7, 8} Twenty-two more articles on chlorophyll followed. They were all combined in a book by Richard Willstätter and Arthur Stoll which came out in 1913. Among the new results were the magnesium content, the uniformity of chlorophyll throughout the plant kingdom, its composition of two components (a and b), the close relationship to the red pigment of blood, and the presence of a complex alcohol, phytol, as part of the chlorophyll molecule. This was purely scientific work, yet it led to many practical applications.

For example, phytol has become a starting material for synthesizing vitamin E, and the corresponding acid (phytic acid) is used in industry.

And yet, after this great success, Willstätter abandoned the field of chlorophyll chemistry and turned to other plant pigments, the yellow pigments in carrots, called carotenes, and those of the flower petals in their rich tints and shades, called anthocyanins. This was mainly carried out at the Chemical Institute of the Kaiser-Wilhelm-Gesellschaft for the Promotion of the Sciences at Berlin-Dahlem from 1912 to 1914. The material for these studies was collected from a large flower plantation on the institute grounds to make sure that the petals used were in their natural state, not altered during transportation or by drying and conserving. A new laboratory method again was essential, this time the specific adsorption on inert carriers as a means of separating the delicate substances from one another.

Once again, this work was abandoned after it had brought highly interesting new results. One very powerful reason was the start of World War I. Although he was not at first directly involved in war work like his friend Fritz Haber, the development of gas warfare resulted in an appeal to Willstätter for protective measures. Within a few months, he completed a gas mask with three layers of absorbents including activated charcoal and hexamethylenetetramine. The use of this chemical remained a secret for many years.

He did not continue the work on flower pigments after he returned to Munich in 1915. "I did not want to give the example of an investigation which required the very greatest consumption of organic solvents. Thus I declined to take up the interrupted work again. However, I doubt that the reason was really so simple. The difficulties could naturally have been overcome in time. Was it not actually the case that the deep darkness of enzyme chemistry was more alluring to me than the detailed work on the chemical structure of chlorophyll derivatives, exploration of nature more than systematic organic chemistry, adventure more than system and synthesis?"⁹

In Dahlem and in Munich he studied how carbon dioxide is assimilated by the green leaf. Isolated chlorophyll cannot do it,

the entire living leaf seemed to be necessary. The work was considered completed in 1917 and published in book form the following year by Willstätter and Arthur Stoll.

From then on, Willstätter concentrated on a new great topic, catalysis, by two different kinds of agents, metals and enzymes.

For the addition of hydrogen to unsaturated compounds, called hydrogenation, Adolf von Baeyer had used sodium amalgam, which develops hydrogen upon the addition of water. Catalytic hydrogenation with platinum metals as catalysts furnished the surprising result that traces of oxygen were necessary for the effect. Willstätter and Ernst Waldschmidt-Leitz had discovered that fact during the Dahlem years. In Munich, the study was resumed. The main effort, however, was on the nature and action of enzymes, which had already played a role in the chlorophyll work. The leaf contains a chlorophyll-splitting enzyme, chlorophyllase, which had to be inactivated in order to obtain unchanged chlorophyll. Now, many other enzymes were extracted from yeasts and leaves and roots. They were purified by the then almost forgotten method of chromatography which Michael Tswett (1872–1920) had published in 1906.

Enzymes were considered as mysterious agents connected with life processes. Willstätter strongly emphasized the view that enzymes are chemical substances. They were, in his opinion, characterized by complex formation with proteins to what he designated as "simplexes," aggregates of substances which acquire special new properties through the aggregation.

In order to produce the special adsorbents for enzymes, Willstätter went far into the field of inorganic chemistry. He found methods for making solutions of silicic acid and for obtaining the hydroxides of aluminum, iron, and tin in chemically specific and defined forms. Here he was often in conflict with authoritative pronouncements of colloid chemists. "When I found something new in organic chemistry, it was accepted as valid. When, however, I entered a neighbouring field, like for example inorganic chemistry, I did not readily find acceptance and willingness from my colleagues."¹⁰

Not all of his colleagues were willing to acknowledge the value of his enzyme work. Henry E. Armstrong remarked, after Will-

stätter's Faraday lecture on enzymes in London, 1927, "May I say that it is a matter of our deepest regret that you have ceased from inquiry into the field of plant pigments."¹¹

Experimental work was only part of Willstätter's activities in the difficult postwar years. The burden of lecturing was great, the care for the students and the institute took much time, willingly and abundantly given. "A researcher who does not let his students watch his experiments, a scientist who does not invite his students to his desk when he writes, appears to me not to be the right kind of teacher."¹²

His efforts found high recognition by his peers in the award of the Nobel Prize (1915), and in the love of his students. However, political events soon caused a drastic decision. The Nazi movement had started with a *Putsch* in Munich. Anti-Semitism grew among the faculty. On three occasions in 1924, when new department heads had to be elected, Jewish candidates were rejected. One of them was Richard M. Goldschmidt, obviously the most outstanding candidate for the chair, held until then by the mineralogist Paul von Groth. Richard Willstätter thereupon handed in his resignation and remained firm in spite of many entreaties. He succeeded in getting Heinrich Wieland to be nominated for his chair. Willstätter remained active in the several scientific organizations that requested his help, but he never entered his institute again. The only assistant who continued his experimental work was Margarete Rohdewald with whom he communicated by telephone and at the writing desk in his home.

The study of enzymes thus continued at a reduced pace. Work in scientific organizations, publications, special lectures, and industrial consultations filled his time. Thus he gave the Willard Gibbs Memorial Address at the American Chemical Society meeting in Chicago, September 14, 1933, and he followed the development of a process for producing sugar from wood, based on his patent of 1913 with Laslo Zechmeister. He declined all the offers of important positions that came to him from universities and industry in Germany, Spain, and America.

When Hitler took over the German government, Willstätter still refused to leave Germany. It was one thing to resign from a professorship, quite another decision to give up one's country. His

friend Fritz Haber resigned from his offices and emigrated. If Willstätter deceived himself about the intentions and practices of the Nazi government, it was not for very long. In March of 1939, after grueling experiences, he finally crossed the border into Switzerland. His former assistant and younger friend, Arthur Stoll, provided a new home for him near Locarno.

Here he wrote the memoirs of his work and life, with many poignant remarks about his friends and colleagues. These memoirs show him as a keen observer not only of chemical substances and biochemical reactions, but also of human life. With Fritz Haber he formed a pair like Liebig and Wöhler, and if the comparison could be carried further, the more impetuous Haber would appear closer to Liebig than to Wöhler in this friendship. Willstätter devoted a memorial chapter to him in the memoirs, as he did to his revered older friend, Adolf von Bayer. In addition, he continued some work on the enzyme system of the muscle, again with the experimental help of Miss Rohdewald. On June 7, 1940, he wrote to Stoll: "Garlic is, besides yeast, the most important and the most widely applicable means for improving the whole metabolism, and, which is not recognized, of the metabolism of the skin in particular."¹³

He continued to be interested in biochemistry, plants, and paintings until his heart began to fail. "I do not notice that my illness requires patience; it only demands some attention, perhaps also initiative. Regrettably, I lack the medical knowledge, and also literature, to understand it more deeply."¹⁴ He died August 3, 1942.

NOTES AND REFERENCES

- 1 Richard Willstätter, "Aus meinem Leben. Von Arbeit, Musse und Freunden," ed. und mit einem Nachwort versehen von Arthur Stoll, Verlag Chemie, 1949.
- 2 *Ibid.*, p. 367.
- 3 *Ibid.*, p. 181.
- 4 *Ibid.*, p. 19.
- 5 *Ibid.*, p. 74.
- 6 *Ibid.*, p. 329.
- 7 *Ann.*, 354, 205 (1907).
- 8 See Ref. 1, p. 174f.
- 9 *Ibid.*, p. 184.

10 *Ibid.*, p. 358.

11 *Ibid.*, p. 332.

12 *Ibid.*, p. 216.

13 *Ibid.*, p. 420.

14 *Ibid.*, p. 433.

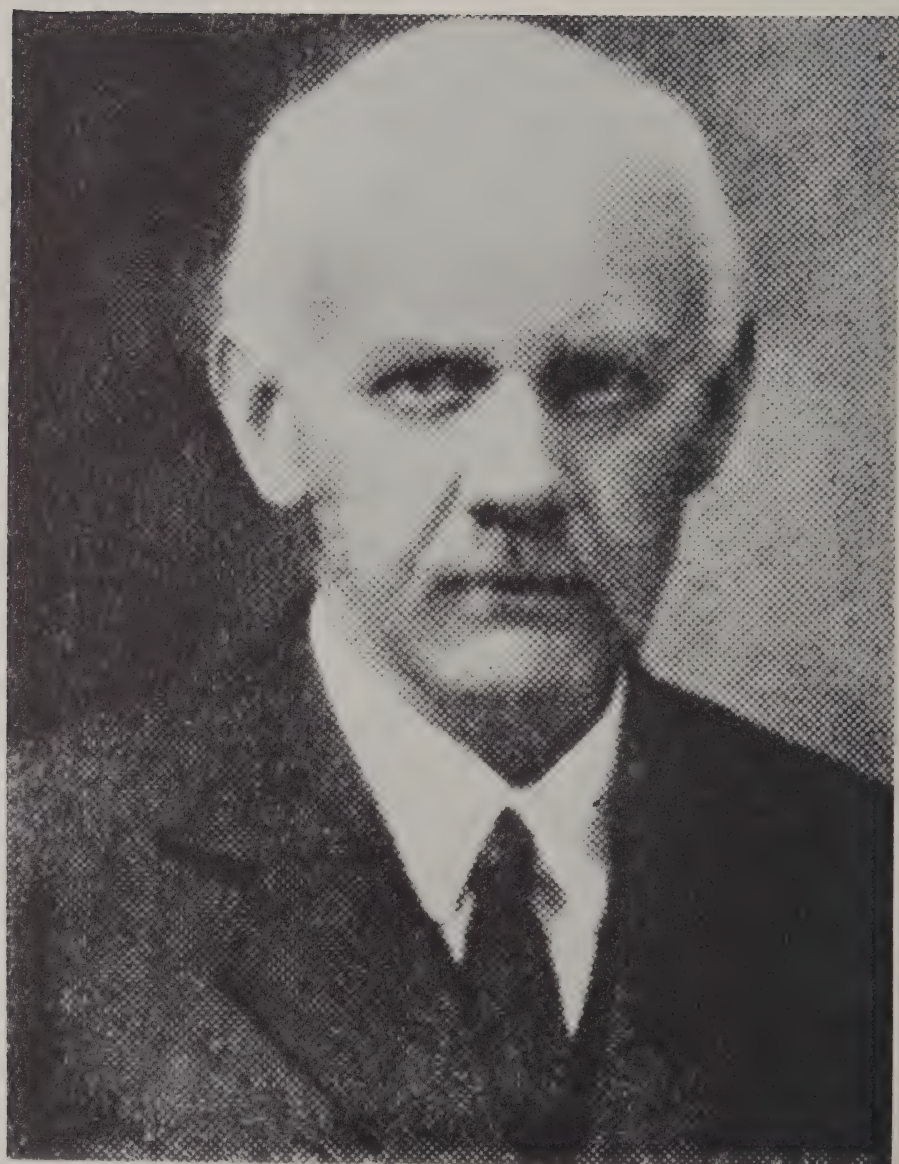
Richard Kuhn, *Naturwissenschaften*, 36, 1 (1949); Sir Robert Robinson, *Obituary Notices of Fellows of the Royal Society*, No. 22, 1953, 609–634, with bibliography.

EDUARD FARBER

.. 97 ..

Nevil Vincent Sidgwick

1873-1952



N EVIL SIDGWICK (born May 8, 1873) was sent to Summer Fields School, near Oxford, for one year from 1885 to 1886, when his parents were living in London. Previously to that he had been educated entirely at home, mainly by his mother, who early imbued him with that love and wide knowledge of botany and natural history which was one of his most marked characteristics and which was to add so much to the interest of his travels. He entered Mr. Scott's House (School Field) at Rugby School in September, 1886, but became a day boy in 1888 when his parents moved to Rugby. He must have been an ungainly boy, physically unattractive and useless at any kind of game. (In later years he became an expert skater, and a competent player of golf, to which he was introduced by one of his Magdalen pupils.) This does not seem to have affected him at all, even in those days when most small boys at public schools had to contend with serious difficulties if their main assets were their brains rather than their athletic accomplishments. Possibly his wit was too biting and his good humor too disarming for his tormentors, if indeed there were any. There is no indication that he had any difficulty in making friends.

Rugby School was then in the forefront of the new movement for the teaching of science at public schools, but there was no concentration on science to the exclusion of literary subjects. Throughout his school career Sidgwick studied classics as well as science. In 1892 he was elected to an open scholarship in natural science at Christ Church, Oxford. Two of his contemporaries were elected at the same time to science scholarships at Balliol and Trinity. Sidgwick applied to the headmaster for the customary half holiday in recognition of these successes, but met with a refusal. The custom was confined to the winners of classical scholarships!

Sidgwick entered into residence at Christ Church in the autumn of 1892. He was fortunate in his tutor, Vernon Harcourt, the Dr. Lees Reader in Chemistry, who was a pioneer in the new domain of physical chemistry, and one of the first to measure the velocity of chemical reactions and to study the conditions that

determine it. The brunt of the teaching of chemistry was borne at that time by the Colleges, and Sidgwick did the whole of his practical work in the Christ Church laboratory. He was placed in the first class of the Honor School of Natural Sciences in 1895. Sidgwick demonstrated in the Christ Church laboratory for a year, and was then elected to a Dixon scholarship which enabled him to go to Germany. He went first to Ostwald's laboratory in Leipzig, in order to acquire modern techniques for the physical study of organic compounds. Unfortunately he fell ill there, and returned to Oxford, where he spent the summer of 1899 investigating the action of alcohol and other organic substances on stannic chloride. He then went to Germany again in the autumn to work under von Pechmann in Tübingen, where he spent two happy and fruitful years, becoming a fluent German scholar, and carrying out a research on derivatives of acetone dicarboxylic acid for which he obtained the degree of D.Sc. in July, 1901. This was published as a dissertation (dedicated to his mother) in Tübingen, but only appeared in the *Berichte* in 1904, the delay being caused by von Pechmann's illness and death.

Before he left Tübingen Sidgwick was elected to a fellowship at Lincoln College, where he went into residence in October, 1901, and remained for the rest of his life. Apart from his unsuccessful candidature for the Dr. Lees Readership in the following year, and a not very serious application for the professorship of inorganic chemistry in 1920, when Soddy was elected, he appears never to have sought any other appointment, or seriously considered any invitation. Lincoln College became his cherished home, and Oxford the center of his life's work.

I well remember my first meeting with Sidgwick in 1905. He was then responsible for teaching the chemists at Magdalen as well as at Lincoln. I had been reading mathematics for a year, and was told at the end of the summer term to go and introduce myself to the man who would be my tutor for my remaining years at Oxford. I called to see him in the rooms which he was to occupy for nearly fifty years. An elderly looking man, almost bald, with a fringe of gray hair, rose and greeted me pleasantly. It was not till long afterwards that I realized he was then in his early thirties. He asked when I had last done any serious chemistry. I told him.

"Oh," he said, "in that case you must settle down to some serious reading in the long vacation." Observing, perhaps, a lack of enthusiasm in my face, he turned to his shelves and picked out a new-looking book entitled "Chemical Statics and Dynamics" by Mellor. "This is an important subject," he said, "but the book is rather too mathematical for me. I wish you'd take it away and see how many mistakes you can find in it." I believe that this was the first time that any senior man had indicated that I might know more than he did about something that was worth knowing, and the first time that anyone had suggested to me that there might be mistakes in a printed book of science. I took it away: an early discovery of a mistake in the first chapter aroused a detective spirit and led me to consult works of reference; and I returned in October with a list the length of which surprised my tutor as well as the author (who wrote a charming letter of acknowledgement), and I learnt a lot of chemistry in the process. This was characteristic of Sidgwick's method of dealing with his pupils. He was a great tutor, except of a few men whom he did not understand and whose difficulties did not appeal to him. Most of his pupils will always remember him with gratitude and affection, although they may find it hard, as I do, to describe the unusual nature of his influence. He did not appear to take very much trouble. He read one's essays casually and uncritically, but with stray illuminating comments. He would spend the rest of the time discussing irrelevant topics, often unconnected with chemistry. He would advise one to go to lectures to see what they were like, but did not blame one for irregular attendance. I did not even regularly attend his own lectures on the organic chemistry of nitrogen; I found it more convenient to borrow the typescript from which he read them, and study it at leisure. He was never caustic about one's ignorance, so long as he detected a desire to improve. He was nearer than anyone else I have known to Stephen Leacock's description of an Oxford tutor in "My Discovery of England":

I understand that the key to this mystery (of an Oxford education) is found in the operations of the person called the tutor. It is from him, or rather with him, that the students learn all that they know: one and all are agreed on that. Yet it is a little odd to know

just how he does it. "We go over to his rooms," said one student, "and he just lights a pipe and talks to us." "We sit round him," said another, "and he simply smokes and goes over our exercises with us." From this and other evidence I gather that what an Oxford tutor does is to get a little group of students together and smoke at them. Men who have been systematically smoked at for four years turn into ripe scholars.

Sidgwick did smoke in those days; a pipe was hardly ever out of his mouth in waking hours except for meals; and by the time he had smoked at one for three years one had a pretty firm foundation of a liberal scientific education on which to build if one had a mind to. But he fell short in one respect: he was not inspiring as an investigator in the years of which I write. His researches, such as they were, were haphazard. At first he continued, in a desultory fashion, his work on the organic compounds of tin, but soon abandoned it without publishing any results. He lost interest in the subject so much as actively to discourage one of his pupils from pursuing it on the reasonable ground that organometallic compounds could be poisonous. But in 1923, when their importance to the study of valency became obvious to him, this objection seemed to lose its force and all his pupils were set to work on them, fortunately without mishap. The fact is that Sidgwick, though accurate, was never an ardent experimenter. He liked to have a band of disciples round him to do most of the work in the laboratory. He was not even very good in selecting topics or advising on methods of research; where he excelled was in the interpretation of results; he could see further than could most of those who produced them. But he had no clear line of work before him until much later. His scientific reputation in 1914 was largely confined to Oxford, and even there mainly to the younger men; some of the older were inclined to regard him as an organic chemist gone wrong. To the outside world of the Chemical Society he was known rather as an acute critic and the author of the "Organic Chemistry of Nitrogen" than for the merits of his original work. The coveted distinction of the fellowship of the Royal Society, for which he yearned, seemed terribly slow in coming; and his closest friends felt that there was some danger of his becoming a disappointed and disheartened man, like his father.

The "Organic Chemistry of Nitrogen" was published in 1910. In the preface Sidgwick wrote: "It is becoming generally recognized that organic chemistry cannot be treated satisfactorily without reference to those questions of physical chemistry which it involves. To attempt a separation of the two is to refuse all the assistance which can be derived from what is the quantitative side of chemistry."

The book was not enthusiastically received by the scientific press; one reviewer went so far as to criticize the author's English—a bold man indeed. It was, however, a great success. The clear, logical, and convincing discussions of controversial matters were of a kind that had never been seen before, and gave the book an altogether outstanding quality. Its educational value was immense. Many of the theories put forward did not survive the passage of time; but the masterly assembly of facts remained invaluable.

The year 1914 was a turning point in Sidgwick's career. He was one of the members of the party chosen to represent the British Association for the meeting held in Australia. This was the first of the many travels overseas which added so much to his enjoyment of life. It was an especial stroke of good fortune for him that Rutherford was a fellow passenger on board the ship. He fell at once under the spell of Rutherford's genius and gaiety. He conceived for him a respect which ripened into a deep devotion in later years. He could not bear at any time to hear even a playful criticism of him; and if anyone was so rash as to differ from Rutherford in print, one felt that Sidgwick would gladly have had the offending article or book burnt by the common hangman! Any pronouncement of Rutherford was right in Sidgwick's eyes; he brought, for instance, the whole weight of his classical erudition in support of Rutherford's suggestion of diplogen as the right name for heavy hydrogen. He felt that this was too serious a matter to be left to the discoverer. However, he took the final decision philosophically: we can at least agree, he said, to denote the new hydrogen by the symbol D.

Perhaps it was Rutherford who supplied the spark that released into its right channels the pent-up energy of Sidgwick's mind. Certainly the curve of his achievements rose thenceforward like the pressure of an explosion. But the period of induction was length-

ened by the war of 1914 to 1918, during which Sidgwick, who was clearly unfitted though not unfit for any normal form of military service, stayed quietly at Oxford, acting as an unpaid consultant to the Department of Explosive Supplies.

In 1922 Sidgwick was elected a fellow of the Royal Society. The distinction did not, in his case, mark the end of his best work for science; it marked the beginning. His horizon extended to embrace the whole of chemistry. He was then forty-nine years of age, full of vigor, and quite unchanged in appearance from what he was twenty years previously. But his friends observed a change in other respects: he became more mellow, more confident, more masterly, and yet more tolerant.

Ever since his first discussions with Rutherford on the way to Australia in 1914 Sidgwick had been interested in the bearing of the nuclear theory of the atom on problems of chemical combination, but he had taken no direct part in the various speculative theories that were put forward after the discovery of the atomic numbers of the elements. The position in 1921 was that there was general acceptance of the view that in the simpler ionic compounds there is a transfer of an electron, or electrons, from the positive to the negative atom, so that each ion is surrounded by a number of electrons equal to the atomic number of the nearest inert gas. This theory, which was first given a precise form by Kossel in 1916, gave a fresh meaning to the century-old idea of electrovalency; but it did not apply to nonpolar compounds. G. N. Lewis, on the other hand, had made an advance of fundamental importance in the same year by suggesting the possibility that in nonpolar compounds atoms could share electrons in such a way as to bring about a more stable grouping of the system as a whole. The most stable grouping, in his view, was one of eight valency electrons arranged in cubic formation. This "octet" theory, which was elaborated by Langmuir and others, received considerable attention; but it was abundantly clear by 1921 that the postulate of stationary electrons was not in harmony with physical evidence. Neither theory, nor any combination of them, could account at that time for the formation and stability of the complex inorganic compounds which Werner had been studying for many years, but in which chemists had taken singularly little interest until he succeeded in predicting

and demonstrating that certain of them could be resolved into optically active components.

This was obviously an unsatisfactory state of affairs, which, in Sidgwick's view, would remain unsatisfactory until more was known about the distribution and function of electrons in atoms. The further information for which chemists were waiting was provided by Bohr's note on "Atomic structure" which appeared in *Nature* in March, 1921, and by the publication of his extended "Theory of Spectra and Atomic Constitution" in 1922. The first fruits of Sidgwick's heightened interest in the subject appeared in his note on "The structure of basic beryllium acetate" and in his paper on "Co-ordination compounds and the Bohr atom," which were published in 1923. In June of the same year Lewis visited Oxford and stayed with Sidgwick. They both attended the meeting of the British Association at Liverpool, where Sidgwick opened a discussion on "The Bohr atom and the periodic law." Their interchange of views, and the publication of Lewis's "Valence and the Structure of Atoms and Molecules" later in 1923 provided Sidgwick with an additional stimulus. He saw his way at last to develop an electronic theory of valency which could be applied to all the known facts without infringing the conditions that physical research showed to be necessary. But to do so it would be necessary to survey the whole field of chemistry.

To this formidable task he now addressed himself. It was a task for which he was pre-eminently fitted. It needed a man with an acute penetrating intellect, an orderly and critical mind, a prodigious memory, an exceptional power of assimilation, and a dogged perseverance. All these qualities Sidgwick possessed; and he buttressed them with a determination to synthesize the sciences of physics and chemistry; never to stretch his inductive logic so far as to reach conclusions which, however attractive to the chemist, would be regarded as untenable by the physicist.

Sidgwick's "Electronic Theory of Valency" was published in 1927. It was rightly said of it when he was awarded a Royal Medal in 1937 that for the first time the most diverse structural phenomena covering the whole field of chemistry were rationally systematized, and that it had more widespread influence on the views of chemists in this country than any other of this generation.

The most original part of this now classic work, of which some 10,000 copies have been sold, was that which dealt with coordination compounds. His original paper on "Co-ordination compounds and the Bohr atom" was indeed a carefully laid foundation stone, now almost lost in the magnitude of the structure that has risen around it. He expounded the results of five years of further study and research in a brilliant Presidential Address to Section B of the British Association at the meeting at Leeds in 1927. Nothing is more illustrative of his powers of induction than his conclusion that the covalency of carbon atoms did not differ fundamentally from the coordination of inorganic compounds. He reached this conclusion after an exhaustive study of all the relevant facts that he could find. It provided a firm basis for the general electronic theory of valency. It followed that the special theory of coordination, which Werner had evolved with so much skill and insight, was unnecessary; and it became clear that the coordinate link is of the first importance throughout the whole of chemistry. His views have since been modified in detail; but their general validity remains unimpaired.

In the last chapter of his book Sidgwick considered in a preliminary way the application of the new principles to the individual elements; and he indicated in the preface his intention to develop this in a second volume. Over twenty years were to elapse before he achieved this ambition.

This highly productive period of his life from 1920 to 1930, during which Sidgwick published the book which brought him international fame, and was also responsible wholly or in part for over forty original contributions to scientific journals, was not without major relaxations. In 1924 he visited Canada with the British Association, and after the final meetings in Toronto crossed the prairies and the Rockies to the West Coast before returning to Oxford. In 1929 he had an even more extended tour to South Africa with the British Association, ending by traveling north to Livingstone by train, then by road to Dar-es-Salaam, and then after two days in Zanzibar sailing home via Aden and Suez.

Toward the end of 1930 he was invited to spend a semester at Cornell University as George Fisher Baker Non-Resident Lecturer in Chemistry. He accepted with alacrity, sailed to New York in

January, 1931, spent a fortnight there, visited Princeton, and settled down in Ithaca early in February, "with every luxury that an American laboratory can supply. Two offices, four telephones, a private laboratory, and a stenographer, all to myself. . . . It is a wonderful place, with a great deal of good work going on, and everybody is most kind, so that I can see that I am going to have a very pleasant time here."

By 1932 Sidgwick had abandoned his intention to revise the "Organic Chemistry of Nitrogen" after writing four new chapters; so when the "Covalent Link in Chemistry" was out of the way he was free to concentrate on volume 2 of the "Electronic Theory of Valency." He made a start on this early in 1935, and in the summer was writing to America: "I have accumulated a lot of material, but I don't want to spend all my time in accumulating and not to live to use it." He soon found that he had taken on a far greater task than he had anticipated. The science of inorganic chemistry had been given a new lease of life through the discoveries and theories of physicists, and it became almost impossible to keep abreast of the flood of papers on new classes of compounds and new elements. And then there was wave mechanics to be reckoned with. Quantum mechanics had been bad enough for a nonmathematician to swallow and digest; but wave mechanics was worse still. It could not be neglected, however. Had it not produced the concept of resonance, which, as he wrote in his introduction to the new edition of the "Organic Chemistry of Nitrogen," is the most important development which structural chemistry has had since it was extended to three dimensions by van't Hoff in 1874?

It was not so much the mathematical as the literary language of the wave mechanicians that he objected to. Resonance was a bad name; for it implies that a molecule is oscillating between two states, which is what the theory denies. It reminded him, he said, of a remark by Mrs. Wilfer, one of his favorite characters in the works of Dickens, of which he was a master: "When I use the term attractions, I do so with the qualification that I do not mean it in any way whatever." However, he did not encourage chemists to rechristen the phenomenon: "For the present we have to accept the terminology of the physicists."

I do not know when the full magnitude of his task broke upon

him, and volume 2 was abandoned in favor of an entirely new treatise. Not before 1939, I fancy, if indeed so early. By then he had revisited the United States six times. America drew him like a magnet. He loved the country; few Americans can have known it so well as he did. Before he died he had visited 46 of the 48 states, and had at least one friend in each. No British scientist was better known in the United States. He was made a Foreign Member of the American Academy of Arts and Sciences in 1938; but by then he had become, so to speak, an honorary American.

The war of 1939 to 1945 was really a blessing in disguise for Sidgwick—or rather for the accomplishment of his purpose. Traveling was out of the question; even visits to London were rare, and held no attractions. Oxford, of all English cities, was the least affected by war, especially if one was a bachelor don living in College. More important still, from his point of view, the gradual cessation of purely scientific work meant that the flood of new information abated, became a stream, and then a trickle. He was able to get abreast of the literature at last. The chief worry now was whether his health, which was steadily deteriorating, would last. It did: his will power and his sense of humor sustained him.

The book, which had grown to two volumes of 750,000 words, was finished at the end of October, 1947, but for a final revision and the compilation of an index.

"The Chemical Elements and Their Compounds" is a monumental work of scholarship. As one reviewer (D. Ll. H.) wrote: "Never before has the content of chemistry been reviewed with such penetrating perception of its structure and such illuminating criticism of its philosophy." Its aim was to discuss in detail the properties of all the elements and their compounds in the light of modern theory; and especially to bring the same order into the study of inorganic chemistry as had existed so long in organic chemistry. No-one had attempted a task of such magnitude before; and it is safe to say that no one else could have achieved it with such remarkable success. It contains nearly 10,000 references to original papers, the greater part of which had been studied and documented, and their essential points stored in Sidgwick's capacious mind, which never seemed to reach saturation. It was not to

be expected that a work of such dimensions could be altogether free from errors and omissions; indeed the book was still hot from the press when chemists from many countries wrote to combine with their congratulations gentle complaints that their own work had been overlooked or misinterpreted. Other criticisms have been made—not without foundation. But few great works of art or scholarship have been free from imperfections; and I can imagine no more instructive task for a young chemist than to compile a list of the mistakes in Sidgwick's last and greatest book. It will take him many months of labor, and into many fields of knowledge, still only partially explored. For the mature chemist it is a mine of information into which he cannot dip at any point without being led to read on by interest in the subject matter and the attraction of the style. Sidgwick's own estimate of its circulation—"judging from the number of enquiries I get about the book's progress from both sides of the Atlantic"—was from 3000 to 5000 copies within three years. Up to date about 9000 copies have been sold. It will be surpassed in time; but it will long remain a standard work, and a pattern for future authors to emulate.

Sidgwick's place in the history of chemistry is assured. His own researches, embodied in a long list of contributions to scientific journals, are not outstanding for originality. He was a natural philosopher rather than a researcher; inductive rather than deductive; a weaver rather than a spinner. He would weave the threads of the discoveries of others into an ordered and harmonious pattern on a grand scale. He exerted a great influence on his contemporaries. His wide interests and knowledge, his forceful and clear speaking, illumined all discussions, whether in private gatherings or before large audiences. He was a most welcome visitor to international conferences, a cosmopolitan in the true tradition of science.

He died on March 15, 1952.

Selections from *Obituary Notices of Fellows of the Royal Society*,
IX, 237-258 (1954).

H. T. TIZARD

.. 98 ..

Marc Tiffeneau

1873-1946



MARC TIFFENEAU was born November 5, 1873, the sixth of eight children. In 1883, he went from grammar school to the Institut Saint-Joseph, directed by the Maristes brothers at Pont-Saint-Maxence. There, he excelled in intelligence and assiduity to the point that the head of the school, a distinguished Latin scholar, gave him additional lessons in Greek and Latin, although this was not the special province of the Institut Saint-Joseph. He was barely fifteen when he started his apprenticeship at the pharmacy Frigaut in Pont-Saint-Maxence while continuing his studies at Saint-Joseph. In 1892, after working at the pharmacy Vigier in Paris, he concluded his apprenticeship and began to study at the Faculté de Pharmacie in Paris. I met him for the first time in that year.

While preparing for an examination, I had gone to the Hôpital du Midi to see the collection of medications, and there I met a small, vivacious young man with a joyous and almost boyish expression, to whom I was drawn by a spontaneous sympathy. Almost every day we met again at the same place. This was the beginning of a friendship which lasted, without a cloud, until, regretfully, my friend died.

After my military service, I started my studies at the School of Pharmacy and renewed my relations with Tiffeneau. The course given by Auguste Béhal (1859–1941), which played such a great role in French chemistry, was attended by about a dozen young enthusiasts, among them Tiffeneau and I, and this brought us still closer together.

During my three years in Germany we remained in continuous correspondence. Then we went into industry, I to Poulenc Frères, Tiffeneau to the Matières Odorantes De Laire, and our scientific collaboration began. I became engaged in the study of the simple amino alcohols, because I was convinced that the natural local anesthetics, cocaine and tropacocaine, owed their properties not to their heterocyclic nucleus, but to the fact that they are benzoic acid esters of amino alcohols. It will be recalled that the amino

alcohols are obtained by reacting amines with chlorohydrines. At that time, around 1902, the number of known chlorohydrines was quite small and, naturally, so was that of the amino alcohols. By applying the method of Grignard to chloroacetone, Tiffeneau prepared for me the chlorohydrine which enabled me to find stovaine (the hydrochloride of amyl aminoethyl-*p*-aminobenzoate, $\text{H}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{COO} \cdot (\text{CH}_2)_2 \cdot \text{NH} \cdot \text{C}_5\text{H}_{11} \cdot \text{HCl}$). Thus, the first industrial application of the Grignard reaction can be said to have been started by Tiffeneau. I might add that when I asked Grignard about the possibility of treating 30 to 50 kilograms of magnesium at one time; he advised against trying such a dangerous reaction in a closed metallic apparatus in which one could not see what went on. In fact, the first trial with 20 kilograms of magnesium was so violent that the apparatus exploded, and I almost finished my industrial career that same day.

We both left industry almost at the same time in order to devote ourselves completely to pure and applied science. The communications between us became even more frequent than before.

Our friendship was still closer after Tiffeneau married my sister to whom I had introduced him as my noblest and dearest friend, a man whom one could trust completely for life and who could best understand her artistic and intellectual interests. Few marriages were more perfect than theirs, and I believe that if I have done any good things in my life, this was the most successful of all.

In 1903, Tiffeneau and I had formed a group of young chemists, called *La Molécule*. Later, at the beginning of the war in 1914, a number of young industrialists joined us. We met once a month exchanging ideas and helping each other in many ways. It was due to this group, of which Tiffeneau was one of the founders and the most active, that the *Société Chimique de France* was able to overcome the many difficulties connected with the war which had almost stopped the development of the *Société*.

We shared a great interest in music too. The composers whom Tiffeneau preferred were Bach, Beethoven, and Wagner. He knew by heart all the quartets by Beethoven and the operas by Wagner, text and music. His tenor voice had a wide register; he read any musical score at sight, singing all the parts in succession. Gradu-

ally, we formed a group of rabid melomaniacs that performed every week at Marc's house, or at mine, or on Sundays at Justin Dupont's where the hospitality was marvelous.

Tiffeneau traveled much, most often to fulfill missions and to attend congresses. He was seen in Rome, Frankfurt, Ghent, Leningrad, Brussels, Edinburgh, Madrid, Zürich, and particularly in Geneva, since he was an expert for the League of Nations. His last great trip, which he undertook in my place with his usual devotion, was across South America in all directions. There he gave a large number of lectures on theoretical chemistry, chemotherapy, and pharmacology. He was greatly helped by his wife who spoke English, German, and Spanish fluently and who, in spite of delicate health, accompanied him everywhere.

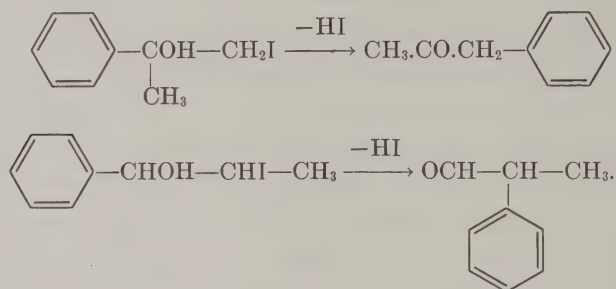
In the year of his death he prepared to go to Basle in order to present a survey of his research on molecular rearrangements. He had also accepted an invitation to lecture in the United States. He gladly sacrificed his health and his convenience in the interest of French science. At the same time he used these travels to increase his already extended knowledge of art. He was familiar with all the museums in Europe. Some of his most beautiful trips were undertaken for the artistic education of his family. Ever since his student days, until 1914, he went to Bayreuth every year.

As I mentioned above, Tiffeneau held many important honorary positions. It frequently happens that such honors and activities connected with them make it impossible to devote time to the laboratory. The lasting interest which Tiffeneau extended to his research and his collaborators is one of the most astonishing facts in his life. Up to the time of his death he published, either alone or with his students, highly interesting papers.

On Pentecost Sunday, 1945, Marc Tiffeneau rose early. He arrived at the railroad station around 8 o'clock because he intended to visit a friend who was sick. As he was walking to the platform to board the train he fell down dead.

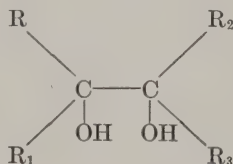
The largest part of Tiffeneau's scientific work was devoted to the study of certain molecular transpositions. This work started in 1902 and continued to the end of his life. A few weeks before his death he presented a summary of this research at the Institut Pasteur.

A molecular transposition generally is any permutation (re-arrangement) within a molecule. When only atoms migrate, the structure of the initially present skeleton does not change. However, the migration of carbon-containing groups (radicals) generally produces modifications of the structure, as can be seen in the following typical examples. Here are two iodohydrines from which one molecule of hydroiodide is removed by the action of silver nitrate:



In the first example, the branched chain is straightened, in the second the straight chain is transformed into a branched one. In both, the radical phenyl changes its place. These transformations in structure can be classified into two groups: In the first group, migration occurs without reactions of addition or diminution, e.g., methyl aniline to paratoluidine, etc. In the second group, the transposition follows upon a reaction of elimination of water, hydrohalogenide, ammonia, or amine. A phase of desaturation is thus followed by a phase of rearrangement. In most cases, only the second phase can be verified by experiment.

The studies which Tiffeneau carried out with so much ingenuity and perseverance belong exclusively to this second group. He and his collaborators investigated almost all the possible variations to be derived from the following general formula in which R, R₁, R₂, and R₃ may designate hydrogen, aromatic and aliphatic radicals, cyclohexyl, and others:



These transpositions are governed by two factors working in the same direction or in opposition, depending upon the nature of the radicals: the degree of affinity and the ability to migrate. They go together for aromatic radicals, and they are in opposition to each other for the aliphatic radicals. The nature of the reagent causing the transposition interferes with the validity of these rules.

This extended work on molecular transpositions required the preparation of many substances for which new methods had to be developed. Particularly in the field of glycols, ethylene oxides, and halohydrines, Tiffeneau, aided by outstanding collaborators, showed his wisdom, perseverance, and profound knowledge of organic synthesis.

Tiffeneau's activities were not all on problems of pure chemistry. He did not forget that he was, at the same time, a chemist, a pharmacologist, and a physician. A great chemist, he also was the greatest pharmacologist of his time. His study of the relationships between chemical constitution and pharmaceutical action was mainly directed to hypnotizing substances, to sympathomimetic and analeptic amines, and to local anesthetics.

One of his outstanding studies that has become a classic dealt with phenolic derivatives of benzylamine, part of which formed his thesis for the doctorate in medicine (1910). He prepared isomers and homologs in the series of hordenine, ephedrine, and adrenaline. He studied analogs of the analeptic substance benzedrine (amphetamine) and local anesthetics related to benzydryl amines. For these, and for derivatives of barbituric acid and of hydantoin, he derived general relationships between chemical constitution and pharmaceutical action.

One of the well-established rules of pharmacodynamics is that amino alcohols become good local anesthetics when they are benzoylated or, quite generally, acylated. However, some amino alcohols themselves have that action (Ogata, 1920). Tiffeneau, Fourneau, Torrès, and Mrs. Benoît studied a large number of benzydryl amines, starting with $C_6H_5-CH(NH_2)-C_6H_4-OR$. Some of these amines are powerful anesthetics, up to twenty times stronger than cocaine; unfortunately, they are also irritants for the cornea and other tissues which makes their use impossible and even dangerous. Tiffeneau and his collaborators stated certain re-

relationships between constitution, anesthetic, and irritating effects. As in many other series of chemical compounds, accessory factors intervene to make general rules impossible.

In the group of barbiturates, the presence of an ethyl radical had been thought indispensable. Tiffeneau introduced other radicals: butyl, isoamyl, hexyl, heptyl, etc. From this research came one of the best sedatives and hypnotics, soneryl (butethal, 5-butyl-5-ethylbarbituric acid).

GENERAL REFERENCES

E. Choay, "Auguste Béhal," in *J. pharm. chem.*, 1, 512-8 (1941).
with bibliography.

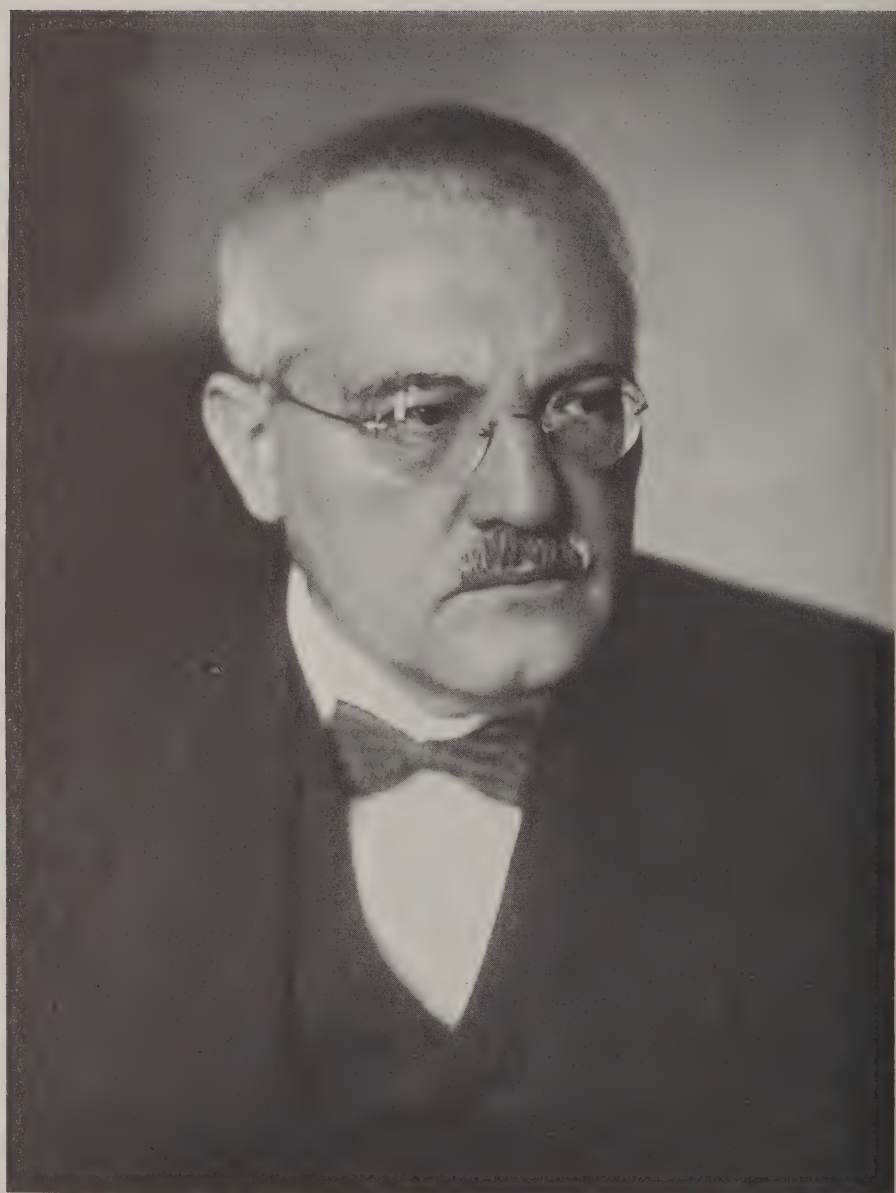
Selections from *Bull. soc. chim. France*, I-5, 905-932 (1948).
Translated by Eduard Farber.

ERNEST FOURNEAU

.. 99 ..

Carl Bosch

1874-1940



ON AUGUST 27 of this year (1949), Carl Bosch would have attained the age of seventy-five years. Since his death on April 26, 1940, great changes have taken place in the world of politics, in the field of natural sciences and technology, and also in the industrial plants established by Bosch. Meanwhile the achievements through which Bosch has enriched industry have remained as a permanent possession of all mankind. The development of high pressure technique, for which he received the Nobel Prize in December 1931, has led to an industry of nitrogenous fertilizer materials, which has attained a magnitude never before imagined, and which is capable of satisfying the demand by agriculture for nitrogen in all countries of the earth for all time. Besides additional new chemical industries, of which that of synthetic methanol with its diversity of additional manufactured products, as well as the metallurgy of carbonyl metals, are to be mentioned only briefly, high pressure technique has realized above all the large-scale industrial production of benzene and middle oils from coal and heavy oils. Much has been written in detail about the history of these developments and the extent of their application; in the year 1920, Bosch himself reported on the development of the nitrogen industry in an extensive lecture at a convention of scientific investigators in Nauheim, and in lectures in Stockholm (1932) and in Oslo (1933) on high pressure technique in general.

Carl Bosch's life work, however, did not consist exclusively of his great accomplishments as a technologist—chemist and engineer—and as director first of the Badische aniline and soda factory and then of the IG Farbenindustrie. Bosch was an inventor and entrepreneur of the first rank, as well as a promoter of research; he was infused with the noblest scientific spirit. He always attached the greatest importance to the complete clarification of technical processes in his plants, and at every opportunity supported, both in word and deed, the cultivation of science, especially of pure basic research. In the years following World War I, he helped research overcome the serious financial difficulties it en-

countered. He was useful to science through the many tasks and suggestions which he gave to the most diverse groups whenever possibilities arose for a thorough scientific treatment and clarification of problems in connection with his technical work.

The love for science, indeed the irresistible urge to get to the basis of all phenomena by scientific means, was apparent in Bosch in his first years of study. The status of metallurgy and mechanical science at that time, to which Bosch devoted himself at first on the advice of his father, did not satisfy the young student at the Technical High School in Berlin-Charlottenburg, not only because he felt that his real interest was in chemistry, but also because the science of materials needed for metallurgy and mechanical science was still influenced by empiricism. The refined methods of the study of metals, as they were developed a few years later, were still unknown or in the beginning stages. "What kind of knowledge is this," Bosch said at a later time in his typical drastic manner of expression, "One calculates the cross section with a complicated formula and then makes it five times as thick so that it will hold up!" Thus it came about that Bosch went to Leipzig and there devoted himself to the study of chemistry at the university. On occasion, Bosch expressed his regret over the fact that technological subjects are taught at technical schools rather than at the universities. Of course Bosch always recognized the achievements of the technical schools, for much that he learned there was of great benefit to him in his subsequent work. If he possessed complete mastery of metal working and of the properties of metals and later was able to contribute considerable practical and scientific progress in these fields, it was chiefly because the basis for this had been given him in Charlottenburg.

His completely scientific manner of thinking and working became evident soon after entering industry, particularly when, in 1909, he was given the task of developing the synthesis of ammonia. Here his actions were guided by the principle that technology must not be satisfied merely with accepting and making use of science for its practical purposes, but that it must contribute to propagating and deepening scientific knowledge in larger fields. He was convinced that this is the only way in which technology could ensure its permanent progress.

In the ammonia plant in Oppau, which was still being built when the First World War broke out, he had constructed a large three-story laboratory which was equipped with all accessory materials, and which was to serve for purposes of pure research as well as for the requirements of the plant. The constant close contact between this laboratory, called the "Ammonia Laboratory," the directorship of which was given to Alwin Mittasch, and the technical works proved to be an excellent means of constantly supplying new tasks for scientific research and thus serving the progress of the newly opened fields. Thus, for example, Bosch stated that we must not be satisfied with the practical mastery of the synthesis of ammonia, but that we must also investigate why this synthesis takes place under certain conditions; why, for instance, iron and molybdenum serve as catalysts while tin and lead do not. Workers in the laboratory also were to occupy themselves with the theory of catalysis; well-known investigators, like Walter Fränkenburger and Rudolf Brill, took part in these projects. The theoretical phase relationships of saline manures, especially of double salts and combined mixed fertilizers, were investigated by Ernst Jaenecke and represented by means of exact phase diagrams. At the Agricultural Experiment Station of Limburgerhof, which was founded in the year 1914 at Bosch's suggestion, Bosch not only instituted a general study of the behavior of nitrogen fertilizers made from synthetic ammonia, but also called for a thorough examination of new nitrogen fertilized materials, such as potassium chloride with ammonium nitrate, ammonium sulfate, and nitrate (Nitrophoska), and, furthermore, of the behavior of the most diverse nitrogen-containing organic compounds, such as guanidin, thiourea, oxamide, formamide, and many others.

As a supplement to this work, a special "biolaboratory" was established in Oppau for the investigation of general questions concerning the growth and nourishment of plants, in which the research extended from the effects of enzymes into the field of medicine. Photochemical studies and investigations on the polymerization of butadiene and macromolecular compounds in general were also included, in addition to further topics, in the work of the Ammonia Laboratory.

The effect, unknown at that time, of hydrogen at high pressure

and high temperatures on the carbon content of steel, which gives it tenacity, had caused serious difficulties in the production of high pressure apparatus for the synthesis of ammonia. This impasse led to the establishment of a large material-testing laboratory for the testing and investigation of metals and alloys with equipment; this laboratory was more complete than any owned by university institutes or by the laboratories of the large steel companies.

It became possible to explain and avoid fatigue phenomena in parts of machines that were under great, and especially pulsed, stress, as well as attacks on the metal structure by the effect of different agents. The construction of steam boilers was considerably furthered by this. By means of constant collaboration with the steel industry, Bosch thus gave valuable stimulation to the metallurgy of iron and steel and their alloys as well as to the utilization of these metals.

Another physical laboratory, designed for an extensive "plant control," with large workshops under the direction of the physicist Paul Gmelin, constructed the most delicate apparatus for measurement and analysis on the basis of physical methods, attaining the highest accuracy. The indication of 1/100 per cent and the triggering of an alarm at 1/10 per cent of carbon monoxide in air should be mentioned as examples of their productive ability. Colorimetric procedures were worked out for the measurement of concentrations of colored solutions, e.g., copper solutions, as well as photoelectric methods for indicating the dew point; analytical methods using qualitative spectral analysis in the regions of ultra-violet and infrared wavelengths using the Raman effect; and roentgen rays and electron diffraction were put to use in the study of metals. Another large laboratory, the "technological testing station," under Prof. Wilhelm Wilke, was concerned with the testing of the engine characteristics of fuels for Otto and Diesel motors.

From the very beginning, after entering the field of technology, Bosch placed great value on measuring everything which could be measured in any way. He owed a great measure of his successes to this thorough method of working, which he also demanded of his co-workers.

Bosch radically departed from the system customary in the

chemical industry at that time of the seclusion of different laboratories and plants from one another; it now became the rule in the individual factories to discuss new advances in colloquia and meetings.

More and more, the policy of giving the public some insight into the newest technical and scientific experiences of the factories was followed, even if there were places here and there in the plants where this was not approved of. Bosch considered it a self-evident point of honor to pay to science a part of the debt of gratitude it deserved for the foundations which had been obtained from it for the establishing of the great factories. Thus a large-scale compromise between the requirements of safeguarding an advantage acquired at high cost and a furthering and strengthening of science which in turn would benefit technology was established. As a consequence, the scientific reputation of the factory, and of industrial work in general, was increased; this involved a publicity potential not to be underestimated.

Several hundred thousand copies of a monthly periodical, "Agriculture and Technology," were distributed to farmers.

Bosch had such high esteem for the significance of thorough scientific working procedures that, even during times of economic depression when other industries began to reduce their research budgets, he maintained the large laboratories and testing institutes in which he saw the indispensable basis of a rational technological method of working. "Today, technology in the best sense is organized science." This was the theme of his acceptance speech which he addressed to the festive gathering after having been awarded the Nobel Prize in 1931.

In October, 1917, Bosch was elected to the governing board of the Kaiser Wilhelm Society and of the Kaiser Wilhelm Institute (KWI) for Chemistry, in recognition of his achievements on behalf of scientific research which he accomplished, in the midst of a very heavy work load, by the establishment of the great Leuna factory and the simultaneous expansion of the ammonia plant in Oppau.

After the war, he devoted himself more and more to supervising the pursuit of research and the training of successors, the

deficiencies in which, as a result of the war years and postwar problems, frequently became clearly apparent in the newly employed academic personnel. Trips to the United States showed him the exceptional means for technology and research in that country, and the general wealth there made the financial distress of the homeland appear all the more pronounced. "We have neither money, nor do we have cheap raw materials, nor do we have enormous sales. All that we have left to us are the people. Therefore we cannot do enough to make it clear to ourselves where our strength lies. It lies only in research, or intensive work." Thus he summarized his experiences in a lecture in Kissingen in 1924. On another occasion, Bosch stated that the training of chemists cannot be too intensive and many-sided, especially since he was convinced that the future rests on the common border fields of several disciplines.

In his essay in the economic journal of the *Frankfurter Zeitung* of April, 1927, Bosch paraphrased the tasks of the chemist in a very comprehensive manner:

Our leading chemists should also be at home in the new frontier of chemistry which was won through the productive development of physics and of physical chemistry in the past decades. I am thinking here of the marvelous development which atomic physics and atomic chemistry have undergone in recent times. The new discoveries about the fine structure of atoms and molecules, about the exchange effect of this material on the one hand and of the electrical forces and electromagnetic radiations on the other hand, will surely lead technology into new fields of thought and work sooner or later. Furthermore it is certain that the new knowledge gained in atomic physics will also be fruitful in photochemistry. This is true for the production of chemical substances whose photochemical formation nature shows us daily in the mighty experiment of the assimilation of carbonic acid by the green plant, as well as for the introduction of new ways of thought into the field of light-sensitive substances, of photographic-chemical technology.

How clearly Bosch anticipated the developments of the future!

In the year 1933, Bosch became a member of the Kuratorium of the Institute for the Physical Foundations of Medicine in

Frankfurt a.M.; in 1935, of the KWI for Physical Chemistry and Electrochemistry in Berlin-Dahlem and the KWI for Carbon Research in Mülheim-Ruhr; and, in the following year, of the KWI for Physics. The institute in Frankfurt, which was taken over in 1936 by the KWG and continued as KWI for Biophysics under Dr. Rajewski, enjoyed special advancement through Bosch. For a long time, he said, he had given considerable thought to the causes for the transformation of organisms and the origin of the geological ages, in which high altitude radiation plays a greater role. He did not allow the objection to stand that the tasks of the institute overlapped those of the Institute of Internal Medicine in Munich. "Furthermore," he added, as we quote here to show a characteristic trait of his way of thinking, "the contact of physics with biology and medicine is so great that not enough institutes can work in this field." His great merits in connection with the institute in Frankfurt found expression in his being named an honorary citizen of the Johann-Wolfgang-Goethe University in Frankfurt a.M. on July 1, 1939. In numerous additional Kaiser-Wilhelm Institutes Bosch occupied leading positions in the administrative and advisory bodies.

Finally, Bosch obtained the highest recognition that could be bestowed upon the leader of an industrial enterprise by the representatives of pure science: he was named to the presidency of the Kaiser-Wilhelm Society on June 22, 1937, the chairmanship of the governing board of the Society had been transferred to him two years before.

In the difficult times between two wars, German science was indebted to Bosch in many respects for extraordinarily valuable support.

His entire love and enthusiasm for natural science found expression in the speech which Bosch delivered on September 16, 1934 in Hannover as chairman of the Society of German Natural Scientists and Physicians during its ninety-third convention. As testimony of a deep, downright philosophical penetration into the nature of research, it is a panegyric more beautiful than has been put into words on almost any other occasion. At the same time it was a courageous and deeply moving cry of despair in view of the

oppression to which the establishing of goals for research was subjected at that time in Germany. He said, in part:

It is inherent in the peculiar character of natural science research, as in each field of science, that it cannot set mental or geographical limits for itself without endangering its goals. Also, it fights for its progress in all philosophical-political situations, because it is timeless in its character. . . . The present limits of scientific research have been pushed far beyond the distance of the starry sky and below the realm of subatomic processes. It is conscious of these limits and, beyond them, sees the path free for metaphysical needs by separating the field of research from that of surmising.

Bosch, the investigator, who was so matter-of-fact and sober in his thinking and very reserved, made it clear that there is a region beyond the boundaries of that which can be explored, where one cannot do research, but merely surmise and revere.

Bosch's comprehensive knowledge and great amiability won for him the highest esteem, an enduring reverence, and in many instances, permanent close friendships. With open-minded foresight Bosch was also interested in research projects which, at the time, were of a purely abstract nature. Einstein's astrophysical observatory in Potsdam was constantly supported by him with considerable contributions which aided greatly in its development. Bosch also had a friendly relationship with Fritz Haber, who provided the scientific basis and the impetus for the synthetic ammonia industry which Bosch created so magnificently. It is to be remembered how energetically Bosch insisted on the carrying out of the memorial celebration for Haber planned by the Kaiser Wilhelm Society, even though the National Socialist Party prohibited the participation of university teachers and of the members of scientific and technical organizations. Bosch not only visited the festivities himself, but also was instrumental, through zealous endeavors in scientific and industrial circles in filling every seat in the lecture hall. Nothing was farther from Bosch's mind—whether in his personal relationships with learned men or in his endeavors toward the support of scientific teaching and research—than to let himself be led by any viewpoints that were not of purely factual nature. If such influences asserted themselves after

1933, they were for him additional cause for taking a stand, with the full power of his being, for that which he considered right and necessary.

Activity in natural science was also a source of relaxation from his many occupational duties. The joy in nature which he had experienced during his school years in Cologne on excursions in the meadows and fields of the nearby surroundings where, among other things, he could collect many interesting aquatic animals in swampy places, later became the foundation for his hobbies, to which he devoted a large part of his free time. Here, too, he did not lack in scientific thoroughness. In Charlottenburg, as well as in Leipzig, he attended lectures and experiments on the lower native animals, mineralogy, petrography, and plant identification as voluntary elective subjects. Later on, when he entered the field of technology in Ludwigshafen, he became an avid collector in the nearby surroundings, in the Palatinate and in the Odenwald, and on his numerous travels in foreign countries—an activity directed mostly toward the collecting of beetles, snails, minerals, and rocks. He entered his findings, and the circumstances of their discovery, in his diary with great accuracy. He established large collections, increased later by purchases, in his house, including in them the diverse fields of his hobbies.

As an indication of the deep knowledge and the sharp power of observation which he acquired over the years, one example merits mention. Once, during an automobile trip to Munich, he had the car stopped suddenly in the vicinity of Ulm. On a slope he had seen a flowering plant which interested him. He left the car and took along a few leaves and a blossom of the plant, in order to identify it at home. He found that it was a tropical plant whose occurrence he could not explain. Later on he found in his books that this tropical plant was indeed to be found in Germany in a few rare locations in the surroundings of Ulm. He was now very happy that he had found such a rare specimen by a glance out of the car, and that he could include it in his herbarium.

Bosch also enjoyed occupying himself in the workshop which he had set up in his house; there, with great skill, he made apparatus for his collecting activities and for physical experiments. He also found recreation and diversion in astronomy and astrophysics,

for which he had an observatory built next to his house in Heidelberg. On clear nights, he often spent many hours in this observatory, making observations and taking photographs.

His last years were characterized by a glaring disharmony between his happy family life and the high esteem in which he was held by the scientific and technological world, on the one hand, and the dismal political developments, on the other, which embittered his life by creating bad moods and gloomy forebodings in him. He repeatedly spoke in almost prophetic-sounding pronouncements about the impending disaster. A peaceful death prevented him from having to experience the actual occurrence of his grim presentiments.

From: *Naturwissenschaften*, 36, 161-165 (1949). Translated by Elisabeth Lanzl.

K. HOLDERMANN

.. 100 ..

John Edgar Teeple

1874-1931



JOHN E. TEEPLE was, in his own words, "an habitual consultant." It was an apt description: he was one of the greatest of the last generation of American chemists and chemical engineers who rendered to their clients personal, professional service. To this rather exacting task he brought sound training in chemistry and engineering as well as an unusual combination of traits and talents, almost bound to guarantee his success in his profession.

He had a passion for problems. Each morning and evening, commuting between his home in Montclair, New Jersey, and his office in New York City, he did the crossword puzzle in his newspaper, and he thoroughly enjoyed piecing together jigsaw pictures, the bigger and more complicated, the better. His favorite extra-curriculum reading was a good detective story.

Out of this abiding interest in all sorts of puzzling problems grew a hobby, surely a strange one for a busy chemical engineer, but one through which Teeple was able, in his own way, to make an unusual scientific contribution. He became deeply interested in the Mayan civilization, fascinated by its curious hieroglyphics and calendar. He never went on a "dig." He never even visited the marvelous ruins in Central America. He became, however, a research associate in this field of the Carnegie Institution of Washington and a regular correspondent with many leading archeologists all over the world. He wrote a scholarly monograph—one of his two published books—that helped to solve some riddles of the Mayan calendar and to correlate it more accurately with our own chronology. A respected reference found in many archeological texts is: "Teeple, John E., *Maya Astronomy*, Publ. No. 403, Carnegie Inst., Washington, 1930."

In addition to his searching curiosity, Dr. Teeple had a high, almost an exalted, sense of professional responsibility. His relationships with his clients were always on an exceedingly confidential basis. Even his closest friends seldom knew the character of the work in which he was engaged nor the firms that were employing his services.

Over and beyond his most famous contribution in the separation of potash and borax from the Searles Lake brines, he did important work in the industrial production of the three mineral acids, in chlorine and activated carbon, in the purification and standardization of C.P. chemicals, in the distillation of hard woods and the utilization of their by-products, in the production of citric and tartaric acids by fermentation, and of naval stores by distillation from pine wood and stumps. The fruits of these researches were garnered in detailed reports to his clients: they were never published. He considered them the property of his clients and he disdained, as he once phrased it, "to build up my personal reputation at the expense of my employers."

John Teeple had a realistic brain. Habitually he penetrated superficialities to get to the core. Hence he was not easily fooled by appearances nor persuaded by plausible argument. His matter-of-fact point of view made him an exceedingly interesting, sometimes a disconcerting, friend but always an extraordinarily valuable adviser. In conference, when the discussion became involved or repetitious, he would suddenly ask, "So what?"—a devastating, or an inspiring, question.

The 1926 Williamstown Institute of Politics was devoted to an appraisal of the world's raw materials; Dr. Teeple was a member of the panel devoted particularly to fertilizer supplies. At one of the general evening sessions, a most attractive little lady read a paper on "Our Vanishing Woods." So dramatically did she picture the ruthless exploitation of our timber resources that she almost dissolved her listeners in tears. She sat down amidst great applause and John Teeple strolled almost carelessly to the center of the platform.

He was a tallish man with a big, loose-jointed frame. His thick shock of hair, prominent nose, and wide mouth, his deeply lined face, were somewhat reminiscent of Abraham Lincoln; like him, he had a winning smile. He propped his right hand on the low lecturn from which she had read her emotional appeal. Leaning forward, he hooked his left thumb in the armhole of his waistcoat and began speaking in his low, penetrating voice.

"Friends," he said, "let us look the facts of our future wood supplies straight in the face."

His distinguished audience shivered with apprehension. Surely now they would learn the worst. Many of them recognized this great chemical engineer, builder of new industries, keen business analyst, outspoken critic of all flubdubbery. The general tenor of the conference had been dismal. Most of its sessions had developed into the gloomy contemplation of a cheerless, comfortless, very hungry future for the bedeviled human race—after we had squandered all of our irreplaceable raw materials.

"Wood," Teeple continued, "is our most ancient and honorable raw material. Man's first fuel was a handful of sticks; his first weapon was a club."

Then he proceeded to show how for most of its seemingly irreplaceable uses wood has already been largely replaced. Coal and oil have become our principal fuels. Wars are no longer fought with clubs and bows and arrows. Wood is no longer the most important material for our buildings, our bridges, our tunnels. Wood is not now a chemical raw material for the production of methanol or acetic acid or acetone. In fact, our chief, apparently irreplaceable, use of wood today is as a source of cellulose which, he pointed out, could be obtained from annual plants. Then he sketched swiftly the tree-farming activities of the Southern paper mills which since that time have so expanded that the kraft paper industry is self-supporting in its wood supplies. It was a masterful job of exposition, beautifully executed.

"Wood," he went on, "is continually disappearing—in the newspaper headlines—bringing modern civilization to an end. But just suppose it did disappear. What would happen?"

"If wood were to vanish from the face of the earth—which God forbid—this horrible calamity would hardly change the trend of modern existence. For if wood were to disappear, I can think of but one important American industry that would be seriously embarrassed. Without wood, I really do not know what would become of the manufacturers of imitation antique furniture."

He grinned broadly and cheerfully at his audience and strolled off the platform amid gusts of wholesome laughter.

Upon another occasion he privately described an ardent crusader for the conservation of natural resources: "The worthy Mr. Blank is just the kind of a near-sighted 'fraid-cat who a cen-

tury ago would have busied himself organizing an Association for the Relief and Succor of Sperm Whales, because, forsooth, our civilization would be impossible without whale-oil lamps. It is the greatest mistake to save anything for your grandchildren, they are not going to need it."

He was quite as sharp a critic of the manufacturer who committed the economic crime of throwing any valuable material on the dump heap, and he became a specialist in wastes and by-products, their recovery and use. Again his approach was thoroughly realistic. He had not use for "waste for waste's sake," but insisted always that a reclaimed material must be employed in some practical process or sold in a profitable market.

All this is, of course, a strictly chemical point of view, and Dr. Teeple was intensely chemical-conscious. He had unbounded faith in the chemist's ability to provide all the necessities for an ever-increasing population in an ever-advancing civilization. He continually emphasized that the dozen odd chemical elements vital to human life on this planet—oxygen and nitrogen, carbon and silicon, chlorine, iodine, and bromine, sodium, potassium, phosphorus—are all abundant in the composition of our globe. He did not live to see the Atomic Age. Had he done so, one can be sure that he would have hailed it (provided we do not blast ourselves into oblivion) not only as a promise of almost infinite power, but also as a pledge of vastly increased chemical knowledge.

"We know what happens in a chemical reaction," he often said. "Oh, but if we only knew how and why it happens!"

How he would have rejoiced in the opportunities laid bare by recent discoveries in subatomic physical chemistry. He was an habitual chemical consultant and an incorrigible chemical optimist.

John Edgar Teeple was born January 4, 1874, on a farm near the little hamlet of Kempton, Illinois, 70 miles southeast of Chicago. His parents, William Harvey and Abby M. (Hinckley) Teeple, were of old New England stock which two generations before had migrated to the Midwest. When he was ten years old he was left an orphan and was brought up by a neighbor. He never talked of his boyhood except to say that, when he was growing up, a farm boy in the Middle West was expected to earn his keep and that he learned very early to pay his own way. He attended the

local public schools and became an omnivorous reader, absorbing an extraordinary cultural background, particularly in history and literature.

In 1888, at fourteen years of age, he began working his way through Valparaiso University. In 1892 he won a B.S. and the following year, a B.A. degree. That same year he became professor of chemistry and physics at Fremont (Nebraska) College, a double post he held until 1898. While at Fremont he met and married Linda Pease. They had two sons, John Hazen and Granger Odell Teeple, and a daughter, Marion, who became Mrs. Earl Hayner.

In 1898 Teeple accepted a position as instructor in organic and physiological chemistry at Cornell with the opportunity to do graduate work. He received a B.S. in 1899 and his Ph.D. in 1903.

Young Dr. Teeple, thirty years old, came to New York in 1904 as director of the Industrial Laboratories. Four years later he hung out his own shingle as consulting chemist and chemical engineer. During 1917-18 he served as interim professor of chemical engineering at Columbia University, but he declined a pressing invitation to an academic career in order to return to his chosen profession as consultant.

For many years he occupied a modest little office in the Chemists' Club Building in East Forty-first Street, New York. From here he served a diverse group of clients: Charles Pfizer & Company, Naugatuck Chemical Company, Niagara Alkali Company, Tartar Chemical Works, J. T. Baker Chemical Company, Darco Corporation, Binns Chemical Works, the Georgetown Chemical Works, the Southern Extracting Company, and the American Trona Corporation, now the American Potash & Chemical Corporation.

Despite his busy professional life, he found time for worthwhile outside activities. For twelve years he was treasurer of the American Chemical Society and between 1917 and 1924, a member of the National Research Council. For two terms, 1920 and 1921, he was president of the Chemists' Club. He was one of the original Board of Consulting Editors of *Chemical Industries* (now *Chemical Week*) and much of his published writing was contributed to this industrial journal. Many of these were short,

pungent, unsigned editorials, but he also wrote articles on the broader aspects of chemical economics.

It is a pity that Teeple wrote so little. His forthright style was arrestingly vivid, his figures of speech always illuminating. He coined the now-familiar phrases "patient money" and "progress by injunction." He always had something to say and he said it not only effectively, but boldly. His only chemical book, "The Industrial Development of the Searles Lake Brines," is unique in chemical literature. Published as one of the American Chemical Society's monographs, it contains 60 equilibrium diagrams, 86 systems of from four to six components, water and the chlorides, sulfates, and carbonates of potassium and sodium, an expert, highly technical mathematical performance. But the book also deals ably with chemical industrial history and applied chemical economics. Furthermore, it sets forth a pragmatic philosophy of management, workday rules for good personnel relations, and far-sighted chemical prophecies, a goodly number of which have already come true.

Because of this slender volume of only 182 pages, Dr. Teeple is best remembered for his work on the separation of the Searles Lake brines. He well deserves to be, for this was not only a notable chemical accomplishment, but it set up a memorable milestone marking an important stage in the growth of a completely rounded, self-contained American chemical industry.

During World War I this country faced three critical chemical shortages. Two were of basic raw materials, potash and nitrate, for which we were dependent upon natural monopolies in Germany and Chili. At that time, the German chemical industry also had a virtual monopoly, technical and commercial, on the organic compounds synthesized from coal-tar intermediates. During the war, nitrogen was fixed from the air, breaking the God-given Chilean monopoly, and through herculean efforts we met our needs for modern explosives, aniline dyes, and coal-tar medicines, laying the foundation for an American synthetic organic chemical industry. But to achieve permanent independence in our supplies of potash appeared to be impossible. By hook and crook we had been able to supply only a fifth of our growing normal requirements for this essential fertilizer and useful reagent. No source, no method of recovery, was found that could compete on either a

cost or quality basis with the remarkably pure potassium salts mined from the Stassfurt deposits. John Teeple's outstanding accomplishment was the breaking of this strongly entrenched natural monopoly.

Potassium can be recovered from many sources and to meet our wartime needs most of these were tapped. The historic method of leaching wood ashes with water which was evaporated in great iron pots (the original pot-ashes) was revived. Potash was recovered from the flue dusts of cement plants and blast furnaces; from the minerals, alunite in Colorado, Wyoming leucite, and the greensands of New Jersey; from beet sugar and molasses wastes; from kelp along the Pacific Coast. The greatest production came from the brine lakes of Nebraska and California.

Insatiable demand shoved the price up from \$.75 prewar to \$6 per unit, that is, per 20 pounds, or one-hundredth of a ton, of K_2O . Tempted by famine profits there were 128 plants producing potash from one or another of these sources when the war ended. Teeple clearly described their dilemma: "Only two courses were open to them; either to succumb, or to make a scientific and technical study of their problems such as they should have made in the first place. Most of them elected the former procedure; it was easier and less expensive to die."

Shortly after the Armistice the German potash companies announced a price of \$.64 per unit. This was less than half the production costs of the most efficient American plants. Obviously the Germans were determined to rewin the world market and they were strategically placed to do so. They were united in a compulsory cartel, the Kali Syndikat, and could act in unison. They knew the American situation and were confident that in opposition to the powerful Farm Block, Congress, despite the war-taught lesson, would not give this infant chemical industry tariff protection. Their quick, deep price cut had just the effect they wanted. Within two years, of the 128 American potash companies only three were operating.

One of these was the American Trona Corporation working the Searles Lake brines. They had called in Dr. Teeple. Already they had junked over 1½ million dollars' worth of unsatisfactory equipment and were rebuilding their triple-effect evaporators, planning

to expand. To gird themselves for the battle the company was re-organized, with fresh working capital, as the American Potash & Chemical Corporation. They had been warned to expect no quarter.

Periodically, throughout hostilities, a representative of Kali, Paul Freudrichen, appeared at the little plant in the heart of the California desert. Plainly he was keeping an eye on a potential competitor, and on one visit he issued an ultimatum swathed in a smiling warning.

"How foolish are your stockholders," he said, "to invest money in any potash enterprise in the United States. Don't you know that as soon as this war is finished the Kali Syndikat and the Imperial Government will absolutely destroy the whole American industry by selling German potash in this country at such low prices as to crush all competition?"

Teeple had been summoned to a very tough assignment. Not only must he effect the separation of the exceedingly complex mixture of native salts much more economically, but the recovered products must be salable. Borax contamination of potash was a fatal handicap in the fertilizer market. Complaints of crop injury by the Trona product, especially to cotton and tobacco in the Carolinas and to potatoes in Maine, had been numerous; back in 1918 the Hubbard Fertilizer Company had brought suit for damages of \$275,000. The case came to trial in Baltimore, May, 1922, and Judge Stanton of the Maryland Supreme Court found Trona blameless. Hubbard had set their own specifications as to borax content and the potash delivered had met their standards. Furthermore, at the first complaints, Trona had shut down, ceased shipping, and at great expense revamped its operation to produce virtually borax-free potash. But the initial prejudice was widespread and had to be overcome. Teeple must maintain and, if possible, raise quality and drastically lower costs.

He first undertook an exhaustive study of the equilibrium data of the 18 consistent salts in the brine. Upon this factual foundation, the triple-effect evaporators were redesigned and the filters were replaced by settlers in order to effect a continuous production of borax and potash. The removal of sulfates and the prevention of the formation of glaserite ($\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$) was much helped by the discovery of the double salt, burkeite (Na_2CO_3 :

$2\text{Na}_2\text{SO}_4$) isolated by his collaborator, William E. Burke. This and the complete separation of borax and potash by rapid cooling of the hot concentrated liquor were vital steps in the operation. The process was not fully perfected in all details until a third new plant was built in 1924.

In 1927, when Teeple was awarded the Perkin Medal, he was able to report that the Trona plant was the largest borax recovery operation in the world and that it was producing virtually pure potassium chloride and selling it at about \$.70 per unit in competition with the German and French mined salts.

This outstanding achievement has overshadowed his other notable contributions to the development of the American chemical industry. He was distinguished, as L. V. Redman said in his medal presentation address, by "his capacity for highly specialized scientific research and his ability as a businessman to hold the confidence of capital till he had turned red figures into black." His greatest contributions were in the perfection of plant processes. Here he was an audacious innovator. Repeatedly he introduced unorthodox design of equipment and novel hook-up of apparatus with amazingly successful results even in operations so standardized that they had become what he delighted to call "family heirlooms."

After a long, painful illness, induced by gallstones, John Teeple died in the Presbyterian Hospital, New York City, on March 23, 1931. He was fifty-seven years old and at the height of his career. In these days of richly endowed research institutions and huge engineering firms with their staffs of draftsmen, lawyers, accountants, and purchasing agents, and all sorts of technical specialists, his individual, personal services seem sadly outmoded, even a bit pitiful. Yet for all its stunning accomplishments, our present-day highly organized research tends to smother individual initiative and to gloss over personal responsibility. It is a healthy antidote to recall the sturdy individualists of the past.

GENERAL REFERENCES

The best material is in his own and the other addresses at the Perkin Medal Award, *Chem. & Met. Eng.*, 34, 122 (1927); *Ind. Eng. Chem.*, 19, 318 (1927).

See also "Who Was Who," I, 1222; "Am. Men of Sci.," 4th ed., 1927; "Dict. Am. Biog., XXI," 682.
Obits, *J. Am. Chem. Soc.*, 53, 61 (1931); *Chemicals*, Mar. 30, 1931, p. 12; *Chem. & Ind.* (London), 1931, 327; *New York Times*, Mar. 24, 1937.
For early history of U.S. potash industry: Geo. W. Stocking, "The Potash Industry: A Study of State Control," New York, 1931, Chap. 13; John W. Turrentine, "Potash in North America," New York, 1943; Williams Haynes, "American Chemical Industry," Van Nostrand, New York, 1945-54, vol. II, Chaps. 13, 14, 15.

WILLIAMS HAYNES

.. 101 ..

Alfred Stock

1876-1946



ALFRED STOCK, born July 16, 1876, went to school at the Friedrich Werder Gymnasium in Berlin from October, 1882, to October, 1894. "As a small boy already I showed my inclination to science. It started with catching salamanders, collecting plants and raising butterflies. It continued with chemical and physical experiments at home." (A. Stock)

In October, 1894, he passed the final examinations with the mark "very good" and received valuable scholarships. They were of great help to him after he started his studies at the University of Berlin in 1894.

Of the two chemical institutes of this university, one was directed by the organic chemist Emil Fischer, the other by the physicochemist Hans Landolt. Alfred Stock selected Fischer's institute. Its laboratories were overcrowded, so that Stock had to wait one year for a laboratory place. While waiting, he attended lectures not only on chemistry, physics, and mathematics, but also on history of art, physiology (Du Bois-Reymond), and history (von Treitschke).

Twice during his university years he used the summer vacations to work in the private laboratory of van't Hoff. Here, Stock succeeded in solving various analytical problems, e.g., the determination of a little alkali in the presence of much magnesium, while taking part in van't Hoff's investigations on the formation of oceanic salt deposits.

Soon Stock became a teaching assistant to Oscar Piloty (1866–1915). Oscar Piloty, the organic chemist, music lover, mountain climber, hunter, sportsman, and son-in-law of Adolf von Baeyer, had accompanied Emil Fischer from Würzburg as assistant and director of the inorganic division and became Stock's sponsor (1898).

The great skill in experimenting shown by Alfred Stock during his studies and work on his doctor's thesis induced Emil Fischer to select him as his lecture-assistant for the winter of 1898 and the summer of 1899.

With financial support from the Prussian Ministry of Culture, Alfred Stock went to Paris in September, 1899. Henri Moissan, then at the height of his fame, had just become the successor of the inorganic chemist and examiner at the mint, Alfred Riche, at the *École supérieure de Pharmacie*.

It was a gay, international little group that Stock met in Moissan's laboratory. America, England, Austria, Norway, Germany, France, and Russia were represented by men who wanted to study Moissan's methods, particularly the handling of his *four électrique*. While working with this apparatus, one was "constantly in danger of losing one's life, either from carbon monoxide which could only escape through the small windows of the basement, or through glowing iron which threatened to fall from the weak resistance wire fastened to the ceiling."

In November, 1899, Moissan began to give the general lecture on inorganic chemistry, formerly presented by Riche. Its clear organization and its elegant, often humorous, rhetorically splendid form provided a great aesthetic pleasure. Alfred Stock was greatly stimulated; his subsequent lectures and speeches were also characterized by superior and elegant eloquence, by clear arrangement of the subject matter, and by a humor that was masterful and, when necessary, ironic.

Moissan assigned to the young scholar the preparation of new compounds from silicon and boron. This was Stock's first encounter with these two elements which were to be the foundations of his scientific fame. First they presented problems of apparatus construction for him. Moissan's electric oven was not suited to this task because it yielded only carbon-containing products. Therefore, Stock constructed his own resistance oven which soon made it possible to produce two compounds analogous to silicon carbide, Si B_3 and Si B_4 . Stock himself admitted that he always particularly liked constructing and improving such tools. His gift in this direction found its highest achievement in the Stock high-vacuum pump.

After attending the splendid Paris Jubilee-World Exhibition, Stock returned to Berlin in August, 1900, and became laboratory assistant in Emil Fischer's new institute.

YEARS OF GROWTH: 1900 TO 1909

The greatest part of the investigations during these years were concerned with the elements phosphorus, arsenic, and antimony from the fifth group of the periodic system. They resulted in an intimate elucidation of their elemental modifications and their compounds with hydrogen, sulfur, and nitrogen. Several publications dealt with improvements in laboratory apparatus. One of them was the vapor-tension thermometer which later on was developed into Stock's tension-thermometer. With the description of the *cuve à mercure*, first introduced by Berthelot and used in Moissan's laboratory, Stock made this tool known in Germany. However, it also became the source of his chronic mercury poisoning which even in these early years caused him headaches, dizziness, and catarrhs.

In spite of many and prolonged experimental studies, he found time to publish, together with Arthur Stähler, a 152-page book "Praktikum der quantitativen anorganischen Analyse" which appeared in 1909. All the figures in this book, as in almost all of his many publications, were drawn by Stock himself. The "Stock-Stähler" came out in a fifth edition, 1941, and in English, Portuguese, Serbian and Turkish translations.

On April 1, 1906, he was promoted to head of the division, and a few days later he received the title of professor. He was married on August 21, 1906. In July, 1909, he became full professor and director of the new Institute of Chemistry at the Technische Hochschule in Breslau.

THE BRESLAU PERIOD: SEPTEMBER 1909 TO
FEBRUARY 1916

In Breslau Alfred Stock started on the exploration of the boron hydrides with a series of studies which continued for a quarter of a century. The plan for this work dates back to 1900, after his return from Paris. At that time he had begun to ask himself whether boron, the neighbor of versatile carbon in the periodic system, really was as monotonous and tedious as was generally assumed. Specifically, the question was whether the chemical

affinities of boron were restricted to strongly negative elements, like oxygen and chlorine. Would it be possible to detect hidden inclinations to other partners, perhaps even to build up a boron chemistry similar to the carbon-based organic chemistry? The first five studies on boron, carried out in Breslau (1912–1914), showed that this “brittle” element possessed a rich “personality” which, however, it made accessible only to the chosen few.

By decomposing magnesium boride with acid and separating the gases so obtained by liquefaction and fractional distillation, B_4H_{10} was discovered as the first liquid boron hydride, and its physical and chemical characteristics were measured. Upon heating, it formed B_2H_6 , subsequently proved to be the simplest member of the borohydride series. Thermal decomposition of B_2H_6 yielded $B_{10}H_{14}$, a crystalline compound. Studies of the reactions with alkali and halogens led to the knowledge of hypoborates and halogenated borohydrides. Besides, there were indications of other derivatives and modes of reaction.

This work was temporarily interrupted by the outbreak of war in 1914. It also appeared necessary to study the silicon hydrides which were admixed with the boron hydrides and made their purification very difficult. Thus, the last borohydride publication from Breslau (1914) was continued nine years later in Berlin (1923), and the interim was filled with 16 publications on silicon hydrides (1916–1923), during Stock's Berlin period.

Other work in Breslau was concerned with inorganic carbon compounds, carbon subsulfide, C_3S_2 , carbon sulfotelluride, $CSTe$, and carbon sulfoselenide, $CSSe$. Stock returned to carbon subsulfide, a terribly irritating substance, during the war when he was charged with a study of its effect as a war gas. It proved active in very small quantities. A practical application was prevented by its great tendency to polymerize.

MASTER YEARS, BERLIN: MARCH 1916, TO SEPTEMBER 1926

In April, 1916, Stock took over Willstätter's laboratory at the Kaiser Wilhelm Institute for Chemistry in Berlin-Dahlem. Unfortu-

nately, Stock had the laboratory available only for a few months, since it was taken over by the "military" Kaiser Wilhelm Institute, under Fritz Haber's direction, early in November, 1916. During this time, Stock, whose chronic ailments of the respiratory organs and increasing loss of hearing, consequences of the then-unknown mercury poisoning, excluded him from military service, moved over to the chemical institute of Berlin University with all his equipment and staff. The end of the war made it possible for him to return to Dahlem and to elaborate the chemistry of silicon and boron hydrides.

By improving the production of silicon hydrides from magnesium silicide and hydrochloric acid he succeeded in obtaining not only the superficially known gases monosilane SiH_4 and disilane Si_2H_6 , but additionally two liquid silanes, Si_3H_8 (trisilane) and Si_4H_{10} (tetrasilane), and the penta- and hexasilanes, Si_5H_{12} and Si_6H_{14} . Halogenation of these compounds with elementary halogen, halogen hydride in the presence of aluminum halogenide, or chloroform led to numerous halogen derivatives.

Reaction with water yielded the group of siloxanes like disiloxane $(\text{SiH}_3)_2\text{O}$, the first gaseous compound of silicon with hydrogen and oxygen (silicomethylether), or prosiloxane SiH_2O , the volatile and easily polymerized starting member of the series (silicoformaldehyde).

With ammonia, halogenated silanes form compounds like the liquid, monomeric silicotrimethylamine $(\text{SiH}_3)_3\text{N}$, or silicoguanidine $\text{Si}(\text{NH}_2)_2\text{NH}$.

Thus arose a silicon chemistry corresponding to organic chemistry in richness. It was mainly a child of the laboratory, but its results were fruitful for industry as shown by the alkyl derivatives of the siloxanes, the silicones.

Research on beryllium also became industrially important and introduced this metal and its alloys into technology. In December, 1919, Hans Goldschmidt (1861–1923), the inventor of the Thermit process, had proposed to finance collaborative work with Stock. He suggested the production of metallic beryllium, which had been discovered by Wöhler in 1828, refined by Lebeau seventy years later, and had been disregarded since then. Electrolysis

of a molten mixture of beryllium, barium, and sodium fluorides at 1300°C . with a water-cooled cathode which was gradually raised out of the melt furnished crystalline beryllium in good yield. A beryllium study group was formed. The price per kilogram was reduced from 200,000 marks in 1927 to 250 marks in 1940.

Parallel to the experimental work ran many organizational tasks which alone would have sufficed to fill the life of a man completely. The number of his honorary positions in professional groups, charitable organizations, committees on education, etc., was great. Without regard to his health, he worked on their many problems. Unforgettable is his help in reshaping German chemistry and supporting young chemists after the First World War. Yet he said he "could have done much more in every respect" if he had not been ill.

The beginning of his mercury poisoning dated back to his school years, when he frequently worked with mercury in his little laboratory at home and obviously laid the foundation for his oversensitivity to mercury. The symptoms became stronger after his return from Paris in 1900. They were aggravated in Berlin (from 1916 on). In 1923 and 1924 he suffered from an almost complete loss of memory. In March, 1924, after an unbearable winter, he discovered, by accident, the sudden illness of his collaborator Dr. Wolfhart Siecke, and recognized the cause of all his symptoms. A very small mercury vapor content in the air (a few thousandths of a milligram per cubic meter) can cause illness upon prolonged inhalation.

After a rest period, he attacked the exploration of mercury sickness from which, as he found, many other scientists (e.g., Faraday, Pascal, Berzelius, Liebig, Wöhler, Hertz, and Ostwald) had suffered. In 1926 he warned the public of the dangers of this volatile odorless, slowly attacking and long-acting metal:

In deciding to report publicly about personal distress—which is itself would not concern others and would not be worth publishing—I am driven by the urgent wish to warn all those who work with metallic mercury most impressively of the dangers of the volatile

metal, and to save them from the harassing experiences that have spoiled a great part of my life.

Thus he starts his deeply moving report. He describes the symptoms, proposes preventive measures, points out the danger of amalgams in dentistry, and describes analogous cases among colleagues.

The prospect of leaving the mercury-infested rooms of the Kaiser Wilhelm Institute and establishing new unobjectionable laboratories contributed to his decision to accept a call as successor of Karl Freudenberg at the Technische Hochschule in Karlsruhe.

THE KARLSRUHE DECADE: OCTOBER 1926, TO AUGUST 1936

In Karlsruhe, he immediately started to establish several laboratory rooms which were models of efficiency and were frequently studied by visitors from many countries. By means of extensive precautionary measures the air in the laboratories was kept free of mercury vapor, although hundreds of pounds of mercury were in use.

In this decade at Karlsruhe Stock's experimental love belonged to the borohydrides and the study of mercury poisoning. First he improved the methods of preparation by using borides other than magnesium boride and acids other than hydrochloric. Then he adapted and elaborated the method found in 1931 by H. I. Schlesinger and A. B. Burg, which consisted of electrical discharges through a mixture of boron halogenides with hydrogen. Research on the reactions with alkali and earth-alkali amalgams enlarged the knowledge of these interesting addition-reactions to compounds like $\text{Na}_2(\text{B}_2\text{H}_6)$, $\text{Ca}(\text{B}_2\text{H}_6)$, $\text{K}_2(\text{B}_4\text{H}_{10})$, and $\text{K}_2(\text{B}_5\text{H}_9)$. Reaction with ammonia yielded, among other compounds, $\text{B}_3\text{N}_3\text{H}_6$ which is isosteric with benzene.

In general he did not think very highly of speculative discussions and theoretical deliberations. "The splendid development of theory must not mislead to contempt for patient experimental work."

To start his offensive against mercury poisoning, it was necessary to develop micromethods for measuring quantities as low as

1/100,000 milligram. Colorimetric methods were not reliable enough. The goal was reached by micrometry of the tiny mercury globe obtained by cathodic deposition on copper wire and vacuum distillation. Analytical studies were amplified by experiments on animals. It was shown that ingested mercury was less to blame than inhaled metal vapor which traveled from the nose to the brain and accumulated in the hypophysis (pituitary gland).

During his years at Karlsruhe Stock was, as always, interested in educational questions. In collaboration with his lecture assistant Hans Ramser and with Carl Zeiss-Jena he developed a teaching epidiascope. It was a universal apparatus, containing an experimentation chamber for the projection of prone or upright objects in incident and reflected light. I vividly remember the impressive production of a small sodium drop by means of Davy's electrolysis of molten sodium hydroxide, which was visible in the entire large lecture hall. Without the epidiascope it could only be shown to a very small group.

At the Thirty-Eighth Congress of the German Bunsen Society in Karlsruhe (May 1933) Stock published a booklet on "The International Congress of Chemists, Karlsruhe, September 3 to 5, 1860, before and behind the curtain." On the basis of old records and letters, found in Karlsruhe, he described the organization and the course of this congress which was to solve the confusion about Avogadro's hypothesis, the theories of radicals and types, the dualistic concepts, and so on. The reader of this enjoyable presentation of the various temperaments and the clashing opinions at the congress will certainly agree with Stock's facetious statement that there were at that time dualists and several "types" and "radicals" among the chemists as well as in the science of chemistry.

In October 1927, he represented the Verein Deutscher Chemiker in Paris at the celebration of Marcelin Berthelot's one-hundredth anniversary. From February to June, 1932, he was guest professor at Cornell University under the George Fisher Baker Nonresident Lectureship in Chemistry. This gave him a welcome opportunity for collecting his experimental work on "Hydrides of Boron and Silicon" (Ithaca, 1933).

During all these successes, representative duties, and honors

ALFRED STOCK

Stock's health continued to worsen. In addition, he had increasing difficulties with the political party influences in education. Thus he decided to ask for his retirement, and it was granted to him, effective October 1, 1936.

In September 1936, he returned with his family to Berlin-Dahlem.

IN RETIREMENT: SEPTEMBER 1936, TO AUGUST 1943

In small laboratories in Dahlem he continued his research on mercury. The micrometric method of mercury determination was improved to such a degree that the quantity of the metal in a monomolecular film of HgCl_2 on $1/20$ square centimeters (0.01 millionth of a gram) became reliably measurable. The chemical path of mercury poisoning was thoroughly investigated, confirming the previous results.

From 1939 on Stock was plagued by hardening of the muscles (myogelosis). In May 1943, he discontinued his laboratory activities in Dahlem because the two small rooms at the Kaiser Wilhelm Institute were needed for war work. With his wife he moved to Bad Warmbrunn in Silesia, into the house of his brother-in-law.

THE LAST YEARS IN BAD WARMBRUNN AND AKEN: SEPTEMBER 1943, TO AUGUST 12, 1946

Toward the end of February 1945, the advance of the Russians came closer and closer. Alfred and his wife had to leave Warmbrunn in the midst of war confusion, an enterprise beset with unspeakable difficulties because of his greatly impaired mobility. He sought refuge with his old collaborator and friend, Ernst Kuss, who, having been bombed out in Duisburg, had obtained emergency quarters in Dessau and was working, with his staff, in the I.G. magnesium plant in nearby Aken. After four days of the most exhausting train rides with thirteen changes, loaded with the last remains of his possessions, he arrived with his wife in Dessau. Here, his friend Kuss received them with loving care. Because of

the destruction of Dessau they had to move to barracks in Aken.

In January 1946, he gave again a first lecture on boron chemistry before the chemists of I.G.'s plant in Bitterfeld. On February 1 he wrote an urgent appeal to the authorities: "Save the German chemistry!"

He died in the early morning of August 12, 1946.

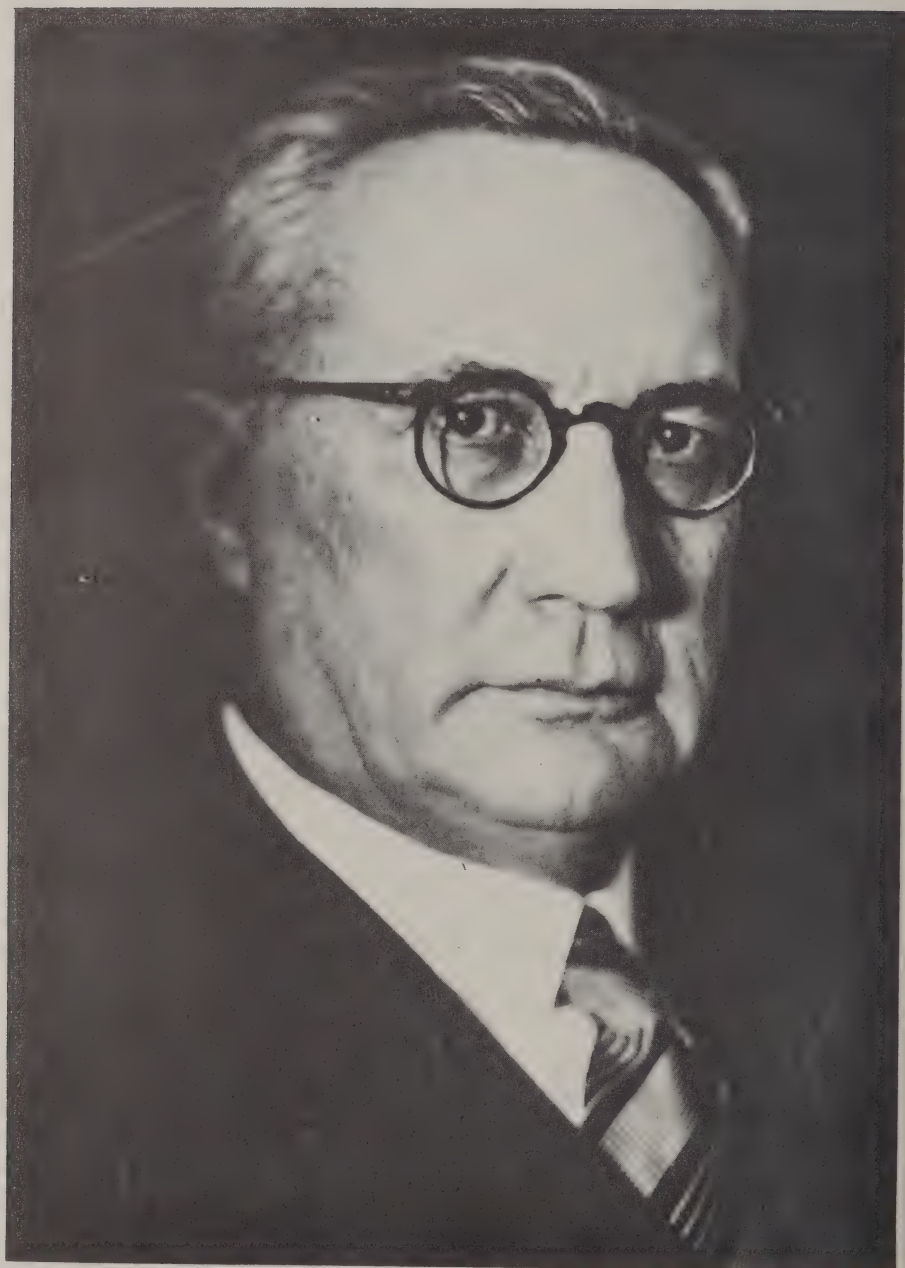
Selected from the biography by Egon Wiberg, *Chem. Ber.*, 83, XIX (1950). Translated by Eduard Farber.

EGON WIBERG

.. 102 ..

Franz Fischer

1877-1947



FRANZ FISCHER spent his childhood in Freiburg i. Breisgau where he had been born on March 19, 1877. His main interests at the gymnasium were chemistry and physics, with little love of languages. After his graduation in 1896 he decided to study electrochemistry, after an interlude of one year in military service.

As a student in Munich, from October, 1897, on, he was anxious to complete the requirements quickly so that he could follow his own ideas. For his doctorate work, under Karl Elbs (Giessen), he studied the chemical events in the lead-acid storage battery. In a few months he had the experimental confirmation for a theory proposed by Elbs. The thesis was quickly completed, and at Christmas, 1899, he surprised his parents with the news that he had acquired the title of doctor.

To reward him for his quick and successful conclusion of university study, his parents permitted him to spend a semester in Paris, doing research under Moissan. There Franz Fischer learned to work with the electric oven and to prepare metals and their carbides.

After an interim course at Wilhelm Ostwald's institute in Leipzig, he went to Berlin and worked in Emil Fischer's institute. Since a paid assistantship did not become available, he accepted a position with an industrial firm at Freiburg. Soon he became convinced that he would not be happy in industrial work, and that scientific research was his field.

He began his academic career at the physiochemical institute at Freiburg. His research centered around electrochemistry.

In 1904, he returned to Berlin, this time as an assistant in the inorganic division of Emil Fischer's new chemical institute. His teaching duties left him time for research. Among other things he discovered an explosive nitride of cadmium formed by exposing the metal in liquid nitrogen to electrical discharges. Of technical interest was his method of depositing iron electrolytically in any thickness; such iron is characterized by ductility and good magnetic properties.

In 1908 he obtained the title of professor and became head of

the department which Alfred Stock had directed. Three years later, he accepted full professorship of electrochemistry at the Technische Hochschule in Berlin-Charlottenburg. There he started work on electrochemical reactions under pressure. By cathodic hydrogenation, he produced hydrogen peroxide with oxygen, formic acid with carbon dioxide. Whereas hydrogen peroxide had so far been obtained only in aqueous solutions, he synthesized pure hydrogen peroxide, using dark electrical discharge and cooling in liquid air.

Through Emil Fischer's interest in this work, Franz Fischer was invited to direct the new institute which the Kaiser Wilhelm Gesellschaft planned to erect in the Ruhr valley. This institute was to be devoted to the study of coal on a purely scientific basis, as the president of the Kaiser Wilhelm Gesellschaft declared in the opening ceremonies on July 27, 1914, a few days before the First World War broke out. In his autobiographical notes, Franz Fischer included a chapter on "scientific freedom" in which he stated that during his term of office he always had the necessary freedom in selecting his objectives and his collaborators. That this scientific freedom of the institute had not always remained undisputed he showed by a few examples, but he gratefully recognized the protection of the institute by the governing agency.

The results of work done at the institute are presented in 12 volumes of "Gesammelte Abhandlungen zur Kenntnis der Kohle" (collected papers on coal research), supplemented since 1936 by the journal *Brennstoff-Chemie* founded and edited by Franz Fischer.

During the first years of operations, the work was dominated by questions of raw material supplies resulting from the war. Thus, Franz Fischer had to delay his intentions to study the conversion of coal or heat into electricity by a direct path. Research on this subject remained very limited later on when again other subjects took precedence, particularly the synthesis of hydrocarbons. The war of 1914 to 18 had drastically demonstrated Germany's lack of natural petroleum and the necessity of providing other sources of motor fuel and lubricants. Such sources could be found, if at all, only in refined coal. In this direction lay the first comprehensive work at the institute.

All important types of German coal were studied as to their suitability for producing tar by low temperature carbonization. Another problem that Franz Fischer and his collaborators attacked early, and to which they returned again and again, was the extraction of coal by means of solvents. Under elevated pressure, and especially with benzene as the solvent at 270°C ., the yields in extracts were many times those obtained at atmospheric pressure. Particle size influences the course of the extraction. By fine grinding the yield can be greatly increased.

Many publications by Franz Fischer and his collaborators are devoted to the problem of the origin of coal. He emphasized the decisive importance of biological processes to which other scientists did not give due prominence. On the basis of experimental work, carried out together with Hans Schrader, Fischer formulated the so-called lignin theory, according to which the biological decomposition of plant materials consumed mainly the cellulosic part and thus left the more resistant lignin to be transformed into humus coal.

The numerous chemical and biological investigations on this subject at the institute did not remain unchallenged as to their conclusions. Whether or not the lignin theory, in its original form, is correct or has to be modified, the experimental results obtained in this connection are valuable for our chemical knowledge of coal.

The hydrogenation of coal under high pressure, initiated by Friedrich Bergius, was the subject of detailed studies at the Mülheim Institute.

The use of coal in fertilizers was also studied, and best results were obtained with lignitic brown coal pretreated with ammonia. Biological gas reactions and biological purification of illuminating gas to remove poisonous substances were investigated. Synthetic resins, called Kolonit, were produced from lignites. Mobile generators of motor fuel from solid fuels were constructed.

The conversion of methane into more valuable hydrocarbons was thoroughly investigated. Reactions at high temperatures at precisely regulated temperatures and time periods led to acetylene under reduced pressures, to benzene at normal atmospheric pressure. Acetylene was also obtained through electrical discharge. Another way was the production, at relatively low temperatures, of

carbides, e.g., of barium, with methane, and their decomposition, again, to acetylene.

The high point in this research was the catalytic hydrogenation of carbon monoxide. This work of the institute under Franz Fischer achieved scientific and technical success of world-wide importance. Systematic experiments on the hydrogenation of carbon monoxide began at Mülheim after the war, starting from the thought that besides the high-pressure hydrogenation undertaken by Friedrich Bergius, only the gasification of coal and the conversion of the gases could lead to the desired liquid and solid hydrocarbons. First there were attempts to use pressure and catalysts to produce salts of formic acid and then to decompose them. Then, in 1925, the synthesis of hydrocarbons at ordinary atmospheric pressure was found by Franz Fischer and Hans Tropsch.

Ten years of intensive work were necessary before this process was ready to be taken over by industry (Ruhrchemie A.G., Oberhausen-Holten). The problems comprised the manufacture of the gases for synthesis, extremely fine purification, disposal of the heat of reaction, and development of highly active catalysts. During these ten years there occurred times of standstill in view of apparently overwhelming difficulties when everything depended upon untiring continuation of efforts to find the solutions. Franz Fischer remained unerringly persistent and imparted this spirit to his collaborators. On November 16, 1934, he summarized the development of hydrocarbon synthesis and ended with the communication that Ruhrchemie A.G. had decided to build a large pilot plant.

Between 1935 and 1939, six synthesis plants in the Ruhr valley and three in other parts of Germany came into existence and produced an annual maximum of 600,000 tons of primary products. Outside of Germany too, several Fischer-Tropsch plants were erected.

Work on the further development of hydrocarbon synthesis continued after 1935; the progress was important. I mention only the synthesis under moderate pressures with cobalt catalysts, the peculiar synthesis of mainly hard paraffin with ruthenium catalysts, and finally the use of iron catalysts. A new type of carbon monoxide hydrogenation was found with oxidic catalysts; it was called

isosynthesis. A vast field of research was the detailed analytical investigation of the primary products obtained by synthesis and their further refinement. Lubricating oils of exceptional quality were thus produced. New ways led to special high-grade fuels required for the new motors.

There is scarcely a topic of chemical elucidation and upgrading of coal to which Franz Fischer did not make a contribution. He had no periods of scientific unproductivity during his entire life. For his collaborators, it was sometimes not quite easy to follow experimentally what he frequently thought up during the night hours. Gifted with thorough human knowledge, he was able to attract and to train many young chemists and engineers as well as able technicians.

In lectures and publications, Franz Fischer regularly reported the new results obtained at the institute, always pointing out the contributions of those who participated in the work. He also encouraged his collaborators to publish experimentally completed themes, in order to make the results available to the public.

He was opposed to interferences by past regimes. He energetically opposed every political dictate.

Because of the excellent reputation of the institute, many foreign colleagues came to visit Mülheim. Franz Fischer cultivated these relationships and frequently visited foreign countries to lecture at international congresses. After the Second World War, the institute received many signs of friendliness, due mainly to the high regard for Franz Fischer. He received the Lord Melchett Medal of the British Institute of Fuel and many other distinctions.

He found his recreation in sociability and close contact with Nature. From his youth he was inclined to catarrhal attacks, and he counteracted them most effectively by long journeys at sea. He came to the United States three times.

After 1943, he lived in retirement in Munich where his wife had moved two years before. In Munich he intended to lecture at the Technische Hochschule where he was an honorary professor. This plan was prevented by the war, as his home was completely destroyed in the summer of 1944; his second home had the same fate. Personal grief and sorrow came to him in the same year. His wife died after long suffering, and shortly before that his daughter

and son-in-law were arrested by the Gestapo and brought to the concentration camp at Dachau.

After the end of the war, Franz Fischer managed, after long labor, to found a very modest new home. It is tragic that the inventor of one of the most important processes of modern chemistry had to struggle tenaciously to obtain even such a modest place of living. He was not even allowed to use his automobile, at a time when the Fischer-Tropsch process was destined to produce millions of tons of motor fuel.

All these adversities and sorrows did not discourage Franz Fischer, who found new strength in the pursuit of science. When a company in Regensburg placed a laboratory at his disposal, he accepted the offer and carried out research on lignin.

He died on the first of December, 1947.

GENERAL REFERENCES

Hermann Kellermann, *Brennstoff-Chem.*, 30, 9 (1949).

Franz Fischer, "Leben und Forschung; Erinnerungen aufgezeichnet in den Jahren 1944 bis 1946," Max Planck-Institut für Kohleforschung, Mülheim a.d.Ruhr, 1957.

J. R. Kummer and P. H. Emmett, *J. Am. Chem. Soc.*, 75, 5177 (1953).

From Herbert Koch's memorial lecture, Dec. 1, 1948, *Brennstoff-Chem.*, 30, 3 (1949), Translated by Eduard Farber.

HERBERT KOCH

.. 103 ..

Heinrich Wieland

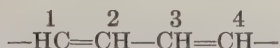
1877-1957



I
w
ri
to
I
c
lo
th
fe
C
re
to
th
in
bo
m
po
—
bo
tic
in
ju
th
ge
3
er
of
C
ph

H EINRICH WIELAND was born June 4, 1877, in Pforzheim where his father was a chemist in a gold and silver refinery. Heinrich started his chemical studies in Munich and obtained his doctorate there in 1901. His sponsor was Johannes Thiele (1865–1918), the originator of a valence theory for organic compounds containing several “double” bonds. It is of interest here to take a look at this theory, because its further development foreshadowed the fate of a basic theory which Heinrich Wieland developed a few years later in a quite different field.

A double bond between carbon atoms, like the one in ethylene $\text{CH}_2=\text{CH}_2$, is not stronger but, somewhat to the contrary, more reactive than a single bond. For example, hydrogen is readily added to form ethane, CH_3-CH_3 . In a sequence of such double bonds:



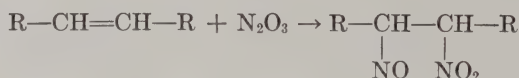
the addition of hydrogen occurs primarily at the ends, saturating carbons 1 and 4, and with the production of a new double bond in the middle. Thiele concluded (1899) that the formula as usually written did not represent this fact, and he proposed a different formulation: The double bonds actually leave

$$\text{—}\underset{\text{|}}{\text{CH}}\text{—}\underset{\text{|}}{\text{CH}}\text{—}\underset{\text{|}}{\text{CH}}\text{—}\underset{\text{|}}{\text{CH}}\text{—}$$

free valences which are mutually bound between the internal two carbon atoms. This causes addition reactions to occur on the outside, leaving one double bond in the middle at carbons 2 and 3. Thiele coined the name conjugated double bonds for such structures. At first, he claimed that all such conjugations should result in the addition of hydrogen, or halogen, on the carbons 1 and 4, instead of 1 and 2, or 3 and 4. However, it was soon found that this is not as generally true as the theory would have required it. Even the simplest of the compounds with conjugated bonds, butadiene, $\text{H}_3\text{C}=\text{CH}-\text{CH}=\text{CH}_2$, does not react exclusively at the carbons 1 and 4; the phenyl-substituted butadienes add halogen predominantly at the

site of the double bond itself. The enticing simplicity of the theory had to be abandoned, but the specificity which had to take its place was gradually recognized to be still more beautiful.

In 1902, Heinrich Wieland began to study the addition of dinitrogen trioxide, N_2O_3 , to single double bonds. He characterized the various ways in which this can occur as having one important aspect in common. Contrary to previous thoughts, the nitrogen is always directly connected with carbon, forming nitroso-nitro compounds:

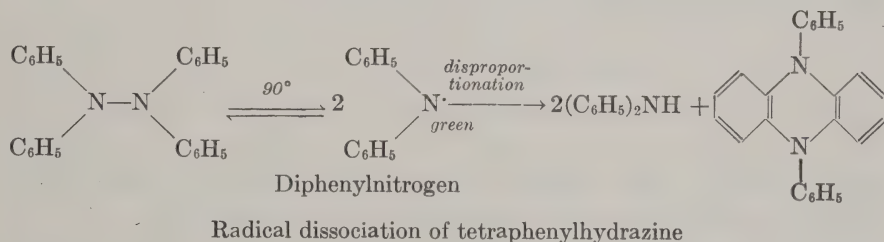


Nitrogen dioxide, in its usual dimeric form N_2O_4 , acts similarly. Wieland concluded that N_2O_3 is constituted as $ON-NO_2$, and N_2O_4 correspondingly O_2N-NO_2 . Theoretically, they are analogous to the halogens $Cl-Cl$ or $Br-Br$. Practically, N_2O_4 should be effective as a nitrating agent with many advantages over concentrated nitric acid.

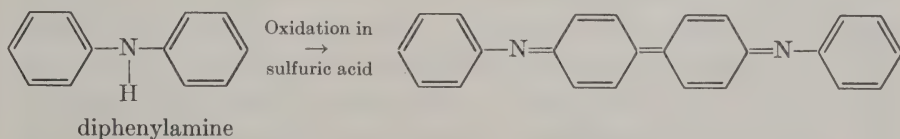
Wieland submitted these results in his habilitation thesis and became a Privatdozent at the University of Munich in 1904. From then on, his work expanded in several directions, most of it on problems requiring great experimental skill and, after many years, yielding results of wide importance with the help of his excellent students and assistants.

One problem of this kind was to explain the reaction which produced a blue color when diphenylamine, dissolved in concentrated sulfuric acid, was treated with oxidizing agents. At first, it was thought that two molecules of the amine lost hydrogen to the oxidant and combined to tetraphenylhydrazine. This was later found to be erroneous; the tetra-substituted hydrazine is formed only when the amine is dissolved in an inert medium, e.g., in ether. In such a solvent, the hydrazine showed a peculiar color reaction which led to a new series of studies. This striking color reaction occurs, in the absence of water, with hydrogen chloride, or with the chlorides of iron, tin, and others known to form complex addition compounds. With tetraphenylhydrazine the color quickly disappears, because the products undergo a molecular rearrange-

ment. When the para positions are occupied by methyl groups, this rearrangement does not occur and the color is more stable. In 1911, Wieland discovered that a similar reaction takes place by simply heating the substituted hydrazines in xylene. A few years before, Moses Gomberg had found that hexaphenylethane breaks apart into two halves, "radicals" containing carbon in the unusual trivalent form, and Wilhelm Schlenk (1879–1943) had just expanded the methods of identifying them as such (1910). It appeared to Wieland that his hydrazines also dissociated into radicals, and that they contained nitrogen in the unusual divalent state. The relative stability of this state is influenced by the nature of the groups replacing the hydrogen atoms of hydrazine $\text{H}_2\text{N}-\text{NH}_2$. A systematic study of the substituted hydrazines showed that the influences are characteristically different from those found for the radicals with trivalent carbon. The analogy, which exists between carbon and nitrogen in this respect, is modified by the differences between these elements.

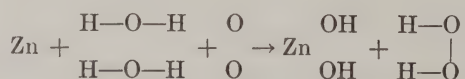


The blue substance obtained by oxidizing diphenylamine in sulfuric acid (1913) proved to be the salt of oxidized diphenylbenzidine, itself an oxidation product of the amine.



At that time, Heinrich Wieland had already begun to study oxidation from a different angle. It had long been a problem how oxidations proceed in the living organism. Since the time of Lavoisier, oxygen was considered to be the active agent in oxidations.

During the nineteenth century, and particularly in its last two decades, various theories were proposed, all relating to "activations" of the oxygen. Johann Ernst Ostwald Schmiedeberg (1838–1921), however, suggested that the explanation should be sought in an "activation" of the substrate, i.e., the substance to be oxidized (1881). Moritz Traube (1826–1894) showed that when a metal like zinc is attacked in the presence of water, oxygen actually combines with hydrogen, and not primarily with the metal; he expressed the reaction by a formula which explains how hydrogen peroxide is formed in this reaction:



From his experiments with platinum metal as a catalyst, Wieland concluded (1912) that hydrogen, not oxygen is activated. When carbon monoxide is "oxidized" to carbon dioxide, water must be present, and it is its hydrogen that is oxidized:



Correspondingly, he considered the catalytic formation of sulfuric acid from sulfur dioxide as a dehydrogenation of H_2SO_3 .

A particularly impressive demonstration for the dehydrogenation theory is the conversion of alcohol into acetic acid without free oxygen in the presence of bacteria. Quinone or methylene blue acts as a hydrogen-acceptor in this reaction.

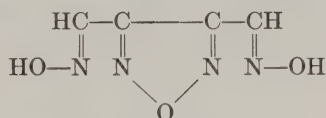
Parallel to this work went an extension from the earlier investigation on reactions with nitrogen oxides. Thus Wieland solved an old riddle which had interested Justus Liebig—the reaction between alcohol and nitric acid, in the presence of mercury or silver salts, by which fulminating compounds are formed. Through his study of nitril oxides, $\text{R}-\text{C}\equiv\text{N}=\text{O}$, and with the analogy he saw between nitrogen oxides and halogens, Wieland found the sequence of reactions which leads from alcohol through its first oxidation product, acetaldehyde, to isonitrosoacetic acid,



and then to fulminic acid,



(1907). This acid polymerizes readily. Liebig's fulminuric acid is a trimeric form of it. Wieland also found the structure of a tetrameric product, isocyanilic acid, and these exist in various isomeric forms.



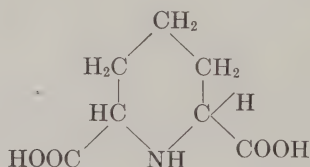
Isocyanilic acid

The year 1912 also brought a publication by Wieland on the chemistry of bile acids. Again the problem had been pursued for a long time, since Thenard, in 1806, discovered a bittersweet substance (picromel) and a resinous, acidic material in bile. Twenty years later, Leopold Gmelin separated 22 different substances from this material, among them cholesterin, cholic acid, and nitrogen-containing acids. These were later hydrolytically split into amino acids and bile acids. Just before Wieland started his work in this field, three particular bile acids appeared to be characteristic: cholic acid, deoxycholic acid, and lithocholic acid. Wieland proved the close chemical relationship among these three by converting them into the same substance, cholanic acid. The steps consisted in dehydration and then addition of hydrogen in the presence of the same kind of catalysts which he used in developing his hydrogen-activation theory of oxidation. The three bile acids were thus shown to differ only in the number of hydroxyl groups attached to the same basic compound; cholic acid has three, deoxycholic two, and lithocholic acid one hydroxyl group. In their basic structure, they are related to cholesterin, which Wieland's friend, Adolf Windaus (1876–1959) had been investigating since 1903.

Research in all these fields, organic nitrogen compounds, dehydrogenation, and bile acids, continued with shifting emphasis when Heinrich Wieland became full professor at the Technische Hochschule in Munich, intensified after the war at the University

of Freiburg (1921–25), and particularly after Wieland returned to the University in Munich, as Richard Willstätter's successor, in 1926.

From 1921 on, Wieland concentrated his research of organic nitrogen compounds on alkaloids, particularly those of the plant *Lobelia inflata*. Predominant among the lobelia alkaloids is lobeline. When methyl iodide is added to this substance, it can easily be transformed into 1,7-dibenzoyl heptane, $\text{C}_6\text{H}_5\text{—CO—(CH}_2\text{)}_7\text{—CO—C}_6\text{H}_5$. Oxidation to the so-called scopolinic acid and other reactions revealed the structure of lobeline.



Lobeline

In a similar manner, the other two groups of alkaloids, called lelobine and lobinine, were shown to differ from the main group in containing a C_2H_5 group for one of the phenyls. Synthesis gave the final confirmation for these structures (1929–1939).

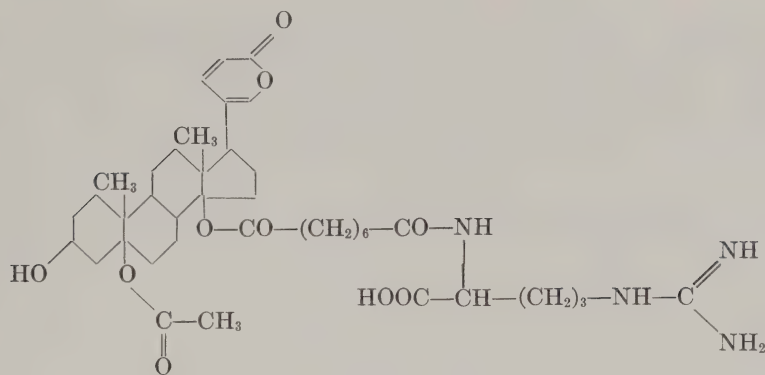
The various kinds of curare, the arrow poison of South American Indians, yielded a substance, toxiferine I, of which 0.3 millionth of a gram was sufficient to paralyze a 40-gram frog (1937-41).

The poison of the mushroom death cup (*Amanita phalloides*) contains several amino acids in an arrangement which Theodor Wieland (b. 1913), Heinrich's son, only recently succeeded in establishing.

At the suggestion of Clemens Schöpf (b. 1899) Wieland turned his attention to the pigments of butterflies, the pterins. They proved to be related to uric acid.

The venom of toads (*Bufo vulgaris*), which acts upon the heart, has an entirely different structure. It is related to the sterols of yeast (1941), and the nitrogen is carried by the side chains, not in the ring structure of the molecule.

Wieland extended his dehydrogenation theory more and more to biological systems, such as the enzymes of bacteria which form acetic acid, and those of yeast, milk, muscle, and plants. He found



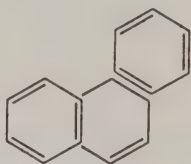
Bufotoxin
Structure of toad venoms

an opponent of great experimental skill in Otto Warburg (b. 1883), who explained that biological oxidations are governed by metals, particularly iron (in rarer instances copper), which act by activating the oxygen. Hydrocyanic acid (HCN) or carbon monoxide inhibits respiratory reactions by "poisoning" the iron surface. The catalytic, oxygen-activating action of blood pigment persists even after charring the hemine because its iron is still present in this charcoal (Warburg, 1921). Wieland thereupon showed that amino acid oxidation in the presence of such charcoal can still be carried out, in the absence of free oxygen, with such hydrogen acceptors as quinone, alloxan, or dinitrobenzene. What the catalyst activates is the hydrogen of the amino group, not oxygen. Warburg countered with experiments on the absorption spectra and the influence of carbon monoxide on them. In light, the effect on respiration is as reversible as the iron compound formation with carbon monoxide. Finally, Warburg had to admit that there are systems in which the substrate, not the oxygen, is activated, and Wieland had to relent insofar as phenol oxidase enzymes of plant materials are concerned.

Warburg received the Nobel Prize for his work on the respiratory enzyme in 1931, four years after Wieland obtained it for his research on the constitution of bile acids and related substances.

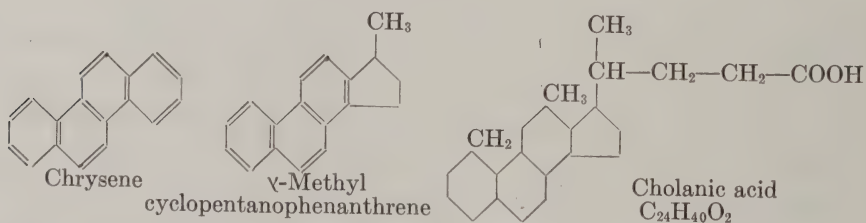
One of the first stations on the long way toward a structural formula for bile acids had been to recognize that cholic, deoxycholic, and lithocholic acid are derivatives of one common acid, called cholanic acid (1912). The next great advance was made by gradual oxidations which attacked the molecules only where

the hydroxyl groups are located (1919). Then, however, an analogy to the behavior of known dicarboxylic acids led in the wrong direction, until it was found that acids of the structure present in the oxidized bile acids were exceptions to the supposed general rule. At the same time, in 1932, O. Rosenheim and H. King concluded from J. D. Bernal's x-ray crystallography of these materials that they are to be formulated as derivatives of phenan-



phenanthrene

threne, and Wieland found a new chemical way which proved such a structure. This structure was also consistent with the results which Otto Diels (1876–1954) had obtained in 1925. He dehydrogenated sterins (sterols) and bile acids by heating them with selenium and found two hydrocarbons: chrysene, and a second one for which the formula of γ -methyl cyclopentanophenanthrene was established in 1934.



Now it only remained to establish the sites of the original carboxyl group and the methyl groups in cholanic acid. Bromination, Grignard reactions, oxidations, and reductions finally permitted to derive the place for each of the atoms and their arrangement in space in the formula $C_{24}H_{40}O_5$ for cholic acid (1936). Wieland may have felt like Adolf von Baeyer when he had experimentally established the place of every atom in the molecule of indigo half a century before. And whereas the knowledge of the indigo molecule was of greatest importance in dye-stuff technology, the results from the investigation of the bile acids

had far-reaching consequences in the biochemistry of hormones.

Like Baeyer, Wieland was able to derive deep insight from apparently simple test tube experiments, and like his great predecessor at the University of Munich, he enjoyed experimenting and teaching to the last years of his long life.

In his memorial lecture before the Chemical Society, delivered on May 8, 1958, Rolf Huisgen said about Wieland's last years: "His sense of justice forced Wieland into a dangerous opposition in the difficult years before and during the war when political tyranny did not spare the halls of science. His uprightness and his personal courage remain unforgettable. He made no secret of his hatred for a totalitarian regime. In defiance of official orders, he protected in his Institute a group of persons persecuted for so-called racial reasons. In 1944 some of his students became involved in a trial for what was then termed high treason. His favorable testimony and his loyalty to the defendants in front of the court demonstrated his courage and his political stand."

"On August fifth, 1957, eight weeks after Wieland's eightieth birthday which was celebrated quietly, a great life ended. A living symbol of human and academic dignity had ceased to exist."

GENERAL REFERENCES

Naturwissenschaften issued a double-number on June 2, 1942, in which Heinrich Wieland's students and friends celebrated his 65th birthday. Elisabeth Dane, Wilhelm Franke, Friedrich Klages, and Clemens Schöpf gave surveys of Wieland's work, quoting many of the over 400 papers with the names of the co-authors.

The *Proceedings of The Chemical Society* published The Wieland Memorial Lecture, delivered before the Chemical Society in London, May 8, 1958, by Rolf Huisgen, in the issue of August, 1958.

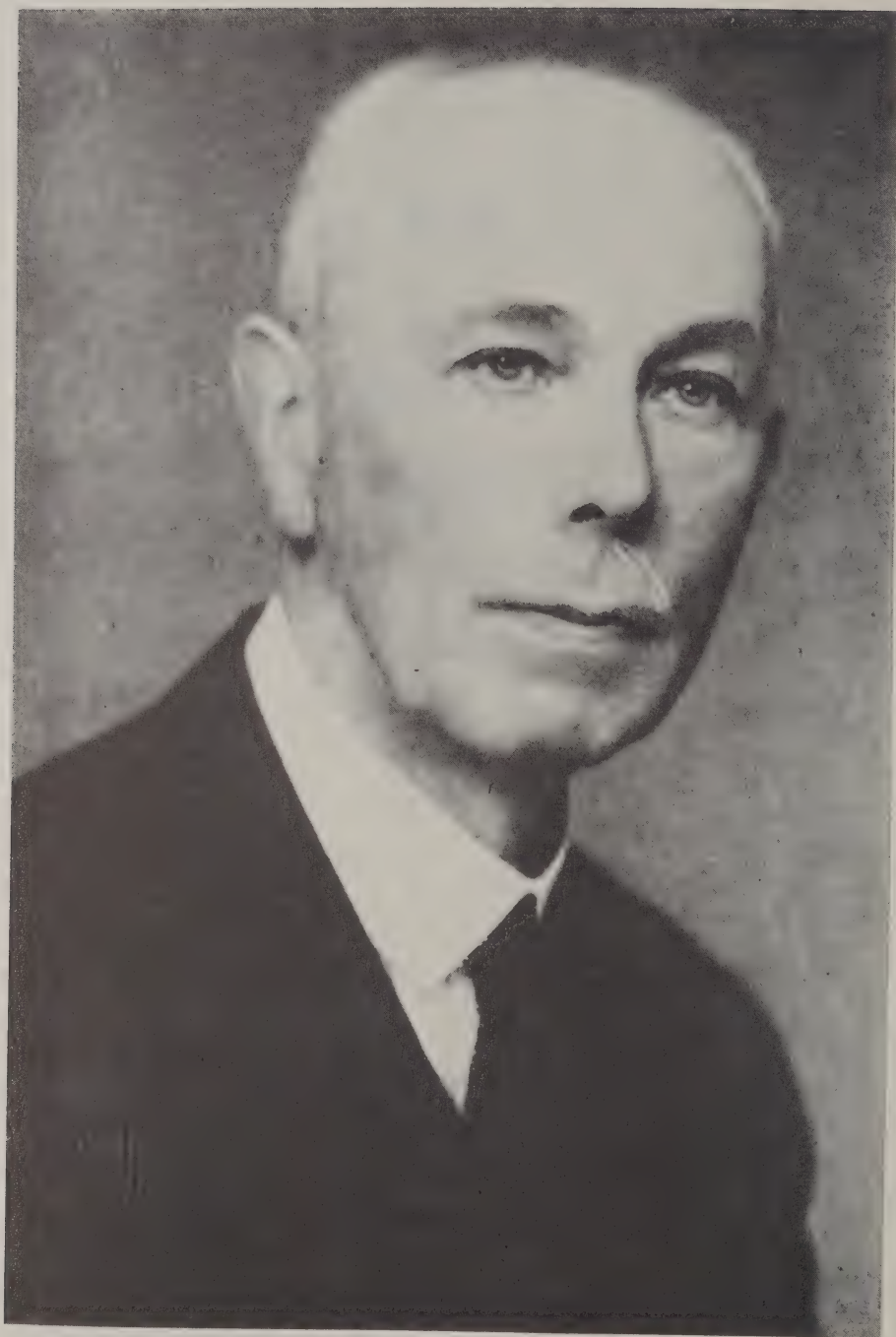
EDUARD FARBER



.. 104 ..

Francis William Aston

1877-1945



ASTON'S name is associated in the minds of men of science with the mass spectrograph and the discoveries concerning isotopes to which it lead. In the history of British physics it is rare that a man's work should thus be associated with an instrument, although it is common enough to be almost the rule among the great names of American science. Although, in fact, in Aston's case the instrument was devised to test a specific theory and not developed for its own sake, it is yet true that Aston's mind was fundamentally that of an instrumentalist to whom experimental methods and actual manual dexterity are a joy in themselves, approaching that to be gained from the results they give. This habit of mind can be traced throughout his life, and the skill of hand that went with it found expression as well in games and in music.

F. W. Aston was born in September, 1877, at Tennal House, Harborne, Birmingham, which is still occupied by a member of the family. He was the second son and third child of a family of seven. From an early age he showed a passion for mechanical toys. After a preparatory education at Harborne Vicarage School, he went for two years to Malvern College, where he began the study of science. He left in 1893, head of the school in chemistry and physics and in the highest mathematical set, to enter Mason College, Birmingham. Here he worked under Tilden and Frankland for chemistry, and under Poynting for physics, of whom he often spoke with affection in later years. At Birmingham, too, he laid the foundation of his skill as a glass blower which was to be so important to him later on. In 1898 he was awarded the Forster Scholarship and worked on the preparation and optical rotatory properties of a complex tartaric derivative, the results of which were published in collaboration with Frankland in 1901. For financial reasons he then took up fermentation chemistry and was engaged for three years at a brewery in Wolverhampton. During this period his thoughts were turning to physics under the influence of the new science that followed the discovery of x-rays.

Quite naturally his interest expressed itself in terms of apparatus. He designed and made a new pattern of the Sprengel pump, and with it exhausted small focus tubes, made from chemical test tubes, in a tiny workshop at home. The Sprengel pump led to a Töpler, also of new design, and he discovered a type of rectifying valve depending on a gas discharge.

In 1903 Aston definitely returned to physics, with a scholarship to the University of Birmingham, as Mason College had by then become, where he worked on properties of the gas discharge, in particular of the dark space. His measurements of the length of the Crookes' dark space and its variation with current and pressure are still classical and appeared in the *Proceedings of the Royal Society* of 1905. Two years after, he discovered the narrow region which appears in some gases inside the Crookes' dark space and is known as the "Aston dark space." Then came a tour round the world, as the result of a legacy, which confirmed him in a love of travel, and especially of ocean travel, that never left him and was the source of much happiness.

In 1909 Aston took the step which, as it turned out, determined his future scientific career, by accepting the invitation of J. J. Thomson to work as his assistant in the Cavendish Laboratory, a post which left him time for independent research. By then Thomson had developed the parabola method of analyzing positive rays, and produced for the first time clear evidence that atoms and molecules were, at least in certain cases, of definite weights for any particular substance. Besides continuing his own work on the dark spaces and measuring the distribution of force in this region of discharge, Aston helped in the further development of the analysis of positive rays. Among the photographs taken on his improved apparatus were some showing a curious effect with neon. Instead of a single parabola due to the atoms of this gas there were two, corresponding to weights of about 20 and 22 units. Isotopes among radioactive substances were already an accepted fact, due to the work of Soddy, and Thomson, not without some hesitation, attributed the two lines to isotopes of neon. The lines were undoubtedly due to neon, since they only occurred when this gas was present. The alternative was to suppose the weaker 22 line to be due to a compound NeH_2 (in this early work it was practically

impossible to get rid of hydrogen). Such a compound was contrary to chemical ideas, but since the method of positive rays had already disclosed several compounds which violated the ordinary laws of valency, the chemical evidence was not very strong, and the decision had to rest on the character of the second line, its variation with conditions, and in particular the appearances of a corresponding line showing a double charge for which there was then no precedent among compounds.

Aston set to work to decide the question. There were two ways of doing so. The first was to try to separate the isotopes if they really existed. The second was to compare the values of e/m of the positive rays with that to be expected from the density of the gas, which gave an atomic weight of 20.2. If the weaker line was due to a compound, the stronger should show a mass of 20.2; if to an isotope, the weight 20.2 must be a mean and the stronger line have a smaller mass, probably about 20. The parabola method was not accurate enough to decide between these possibilities.

Aston started with the first, and as we should now think it, the harder method. At first, indeed, he had some slight success, and an ingenious apparatus for fractional distillation, which of course he made himself, had given a positive result just outside the experimental error when the First World War broke out. During this war Aston worked at Farnborough at the Royal Aircraft Factory, as it then was, as a chemist studying the peculiarities of the doped canvas with which airplanes were then covered, and its preservation by pigments. All the time, however, he was thinking over the neon problem. He lived in a civilian mess known from its location first as "Arnold House" and then as "Chudleigh." Here he discussed physics and the then new quantum theory in its relation to isotopes with Lindemann (now Lord Cherwell), with results which appeared shortly after the war in two joint theoretical papers in the *Philosophical Magazine*. The "Chudleigh" atmosphere was conducive to the spread of ideas; among the others who lived there from time to time being Sir Geoffrey Taylor, Sir Melville Jones, F. M. Green, then chief engineer of the Factory, Prof. E. D. Adrian, W. S. Farren, later director of the R.A.E., D. H. Pinsent, a young man of great brilliance killed during an experiment in the

air, H. Glauert, and the Author. Aston was inclined to be shy in discussing his work, and the ability to do so with men with whom he was really intimate was probably valuable to him. Certainly he always referred to those times with pleasure in afteryears.

The end of the war brought a great disappointment. Two successive pieces of apparatus designed to achieve the separation of the neon isotopes by diffusion failed to do so. It says much for Aston's faith and courage that he was undeterred by these failures, which must have been particularly hard after his previous partial success. The failures were due, not to any error of principle, but to insufficient mixing in the diffusing bodies of gas.

Aston accordingly turned to plans which he had developed while at Farnborough for an attack on the problem by the second method. He devised the well-known apparatus with which his name is so closely associated, in which the ingenious use of electromagnetic focusing of a special type makes great improvements possible in intensity, dispersion, and resolving power. The more delicate parts, such as the slits, of this new apparatus he made himself. The new mass spectrograph, as he called it, was an almost instantaneous success. Not merely did Aston show that neon is indeed a mixture of isotopes, but also that the same is true of chlorine and many other elements.

Aston's discovery was quickly acclaimed. He became a fellow of Trinity in 1920, where he lived ever after until his death. He received the Nobel Prize for chemistry and the Hughes Medal of the Royal Society within two days in 1922; he had been elected a fellow of the Royal Society in 1921.

The earlier work with isotopes was done with gaseous compounds, and many of the metals were missing. In order to get beams of metallic ions, special methods have to be used. Dempster in 1921 analyzed magnesium, and soon after Aston and the author, simultaneously but independently, discovered means of analyzing lithium, which was closely followed by many of the other metals of the early groups of the periodic classification. Later on, Aston succeeded in producing beams of ions from most of the remaining elements, even including the rare earths. In all but a few cases he made the first isotopic analysis.

The original mass spectrograph, now in the Science Museum, South Kensington, analyzed more than fifty elements during its active career and established the whole-number rule. The task of its successor was to measure the deviations from this rule which are so vitally important in nuclear physics, especially for atomic energy.

The new mass spectrograph was accurate to 1 in 10,000. It was characteristic of Aston that to ensure the complete reliability of a battery of 500 small lead accumulators which supplied the field for the deflector plates, he decided to make them himself. He was now concerned with high accuracy, and exerted his ingenuity to devise methods of comparing masses with the utmost precision. These measurements are extremely difficult and in some cases, as might be expected, appreciable alterations had to be made in the results first obtained. By a curious accident a mistake in the ratio of the masses of helium and oxygen stimulated the discovery of heavy hydrogen by Urey and Brickwedde by predicting a larger discrepancy between the physical and chemical atomic weights of hydrogen than in fact exists.

Aston never forgot his early training as a chemist; and his next task, that of determining the relative abundance of isotopes, interested him partly because of its connection with the atomic weights of chemistry. His method was a photographic one, in which exposures were adjusted to make the blackening caused by two isotopes the same or nearly so. His last apparatus, the third mass spectrograph, aimed at an accuracy of 1 in 100,000, and although it did not have quite the resolving power he had hoped for, it achieved valuable results in fixing the mass defects of a number of important isotopes.

Although in the later years work of equal quality was being done in the field of mass spectrography by Dempster, Bainbridge, Neier, and others in the United States, there are few instances in modern science in which the first discoverer of a major field of research has had it so much his own way for such a long time. This is evidence of the technical difficulties involved, not only, or even perhaps mostly, on the measurement side, but also in the production of beams of ions of all sorts of elements with measur-

able intensity. For this, Aston's training in chemistry and in the peculiarities of the gaseous discharge were of the greatest value. But to this training he added that combination of patience and intuition which marks the great experimenter. There is scarcely a research in nuclear physics which does not use his work, directly or indirectly, and usually many times over. The use of isotopes as tracer elements both in chemistry and in biology is only in its early stage, but even now the results are highly important and it is difficult to put a limit on the possibilities of this field. It is true that most of the isotopes used for this purpose are either radioactive or were discovered by the analysis of band spectra, but the method would scarcely be possible without the knowledge of the isotopic structure of ordinary elements which we owe to Aston. Nor is it likely that the rare isotopes of the light elements, such as heavy hydrogen, which his method is not well fitted to discover, would have been found without his work.

Outside his work Aston's interests were most strongly held by sport, by travel, and by music, although any sort of mechanical or scientific device attracted him. In sport he was an ardent skier and made almost yearly visits both to Switzerland and to Norway. He preferred expeditions, often long ones, to trick turns, although he had jumped a little. He liked to do his own climbing and to be independent of funiculars. It was perhaps the greatest grief of his life that a strained heart produced by skiing in the winter of 1934-35 put a stop to winter sports. But skiing was only one of many sports. As a young man he once cycled two hundred miles in twenty-two hours; he was a good lawn tennis player of tournament class, a good swimmer and used to say that the surf-riding he learnt at Honolulu was in many ways the finest sport in the world. He was a golfer well above the average, and the Sunday four with Rutherford, Fowler, and Taylor was an institution. During the First World War he took up rock climbing. On several occasions he led courses classed as of "exceptional severity." Among his miscellaneous activities were photography, bridge, and the special Trinity game of *vingt*, and the collection of Chinese porcelain. He played the piano and violin, but gave most attention to the 'cello.

His love of travel was intense, especially sea travel, and he contrived to combine it with science by going on eclipse expeditions and on British Association visits, although these were by no means his only journeys.

Aston was a man in whom a great zest for life was combined with a simplicity of character almost approaching naïvety. He was interested in people, especially his numerous friends, and probably more interested in things and places. This gift of interest in the outside world made him an ideal holiday companion. The pleasure he clearly took communicated itself to the rest of the party. He was precise in his habits, although it would be unfair to call him old-maidish, for he enjoyed changing from one routine of life to a totally different one. Although a good occasional lecturer, he had no gift for teaching and a few early attempts were not persisted in. He enjoyed scientific meetings, but was essentially an individualist and never attempted to form a school. I think he realized that much of his skill was incommunicable, and that in any event he needed quiet to work his best. His attitude to physics was essentially that of the experimenter and visualizer. He preferred the model to the equation; the concrete to the abstract. The philosophical aspect did not appeal to him. He was a Conservative in politics as in life, and though he would admit that a change might be good, he preferred it to happen as gradually as possible. I last saw him when he received the Duddell Medal of the Physical Society. In a characteristic speech he remarked with some feeling that his researches would never have been passed by any competent planning committee.

In addition to many papers in the *Proceedings of the Royal Society* and *Philosophical Magazine*, Aston's principal published work was his book on "Isotopes," of which the first edition came out in 1922, the second in 1924. In 1933 the name was changed to "Mass Spectra and Isotopes," although much of the material was the same; in 1941 it appeared in final form. He was twice on the Council of the Royal Society, was awarded a Royal Medal and gave the Bakerian Lecture in 1927. He was an honorary member of the Russian Academy of Sciences, and of the Accademia dei Lincei. He received an Hon. LL.D. from the University of Bir-

ningham, and an Hon. D.Sc. from Dublin. He took a prominent part in the work of the International Atomic Weights Committee.

From: *Nature*, 157, 296 (1946).

SIR GEORGE PAGET THOMSON

.. 105 ..

Frederick Soddy

1877-1956



FREDERICK SODDY was born at Eastbourne in September, 1877, and died on September 22 of this year (1956). If he had been an only child many of us who knew him in middle life would have thought him an excellent specimen of the class. His aloofness, his desire to go his own way, his assumption that possibly his word was law, his shyness with others, his desire not to be one of the crowd, would have struck us as almost right. In fact, however, Soddy was the youngest of a large family of boys brought up in Sussex. The mother died early, when Soddy was quite small, and he was left to his own devices in the home. From Eastbourne College, which he left at seventeen, he went to Merton College, Oxford, to read chemistry for his degree after, characteristically, spending a year at University College, Aberystwyth. In 1900, after finishing at Oxford, he went as demonstrator in chemistry to McGill University in Montreal. There he met the great Rutherford, the professor of physics. At that time radioactivity was a major subject of study in physics but no one had an inkling what was its cause. The very brilliant physicist and the brilliant and younger chemist, by their joint work, opened a new chapter in natural science. Their disintegration theory, now so obvious, then so sensational, was put forward in 1902-03. The very heaviest elements were in part unstable. One element could produce another by expelling from its center small portions of its mass or of its electricity. There were three main disintegration series.

After these three fruitful years Soddy returned to England and worked with Sir William Ramsay at University College in London. There he showed spectroscopically that radium produced helium. In 1904 he was made lecturer in physical chemistry and radioactivity at the University of Glasgow where he remained till his appointment to a chair of chemistry in Oxford in 1919. His big research at Glasgow was the proof that carefully purified uranium very, very slowly at first, and later with increased speed, was producing radium. From his results he deduced that between uranium

and radium in the disintegration series there must be a third element, stabler than one and less stable than the other—an important result later confirmed by the discovery (by others) of the element ionium. In Glasgow also he worked on nonseparable radio elements. Concentrating as a chemist mainly on the chemical properties of radioactive material he found that there were far more chemical species showing radioactivity than there were places in the periodic table. He and others showed there were about fifty of the former for twelve of the latter. Soddy triumphed over his contemporaries by coining the word "isotope," now almost a household word. Isotopes are elements chemically identical, and consequently nonseparable, but physically different. The novelty of this idea, thanks largely to the experiments of Aston and the insight of Rutherford, was later shown to have important implications well outside of the narrow field where it was first recognized. The culmination of Soddy's Glasgow period was the formulation of the rules connecting the expulsion of α - and β -particles from a parent radioactive atom and the nature of the resulting product.

In 1914 Soddy was made professor of chemistry at Aberdeen and in 1919 at Oxford. Part of his Aberdeen time was spent on isotopes and part on war work. At Oxford he was very unhappy in his early years. It was his own university; he knew what the college system there was; yet he found himself often at loggerheads with the powerful body of tutors in chemistry. Owing to foolish, quite out-of-date, and long since remedied regulations he found himself at first excluded from all boards and governing bodies connected with his subject. Laboratory instruction, moreover, was only partly a university affair. Half a dozen of the colleges had their own chemical laboratories and were not subject to Soddy's control. His attempts to close these small institutions and concentrate effort in University buildings—the right thing to do—led him to be thought perverse and obstructive. His case was that he was not master in his own department. The tutors thought him cranky. They thought he was always doing unpopular things tactlessly from the highest motives. Even his most adverse Oxford critic, however, would admit "that the worst of Soddy is that he is always three-quarters in the right." Gradually he dropped re-

search in radioactivity and physical chemistry as his interest in social questions began and increased. He became a strident and adverse critic of economics, the businessman, and the financial world. He was undoubtedly unnecessarily violent in his condemnation of what he thought was wrong. As a man of science he recognized that nature and the factory could bring all the good things of life, on its bread-and-butter side, into everybody's home with great ease. All the good things in life, he said, existed in plenty and could easily be put on the highway, thanks to discovery, but the hell's brew of the financial world and the perverseness of the middleman and the banks were robbing mankind of its birth-right. His books and pamphlets on "Cartesian economics," on "wealth and debt," on "money and man," and on "the arch-enemy of economic freedom" made many forget that he had written with great power and insight also on radioactivity, the structure of the atom, matter and energy, and on science and life. His unpopularity with many of his colleagues at Oxford may be illustrated by the statement that although he was a member at different times of three of its Colleges none of them on his early retirement at fifty-nine in 1936 then or later made him an honorary fellow.

Soddy was made a fellow of the Royal Society in 1910 and obtained a Nobel Prize in Chemistry in 1921. He was LL.D. of Glasgow University. He was awarded the Cannizzaro Prize by Rome in 1913. He was a Foreign Member of several continental Academies of Science. In 1908 he married Winifred the only daughter of Sir George and Lady Beilby of Glasgow. They had no children. She died in 1936. Their life together was a very happy one. Soddy might thunder on the platform or curse in committee but in private life and especially in the home he was the soul of courtesy, gentleness, and good manners. He had a fine appearance, tall, fair-haired, Scandinavian—a splendid head. To the Scots of Glasgow and Aberdeen he appeared to be the typical English public-school and Oxford man. Quietness, aloofness, and even superciliousness concealed at times thoughtfulness, kindness, and generosity. Many of his needy pupils remember his generosity to them at the right moment in the days before scholarships and university grants had become common. One of his last acts was to

come to Oxford, knowing he was a dying man, and to give handsome checks to laboratory stewards and assistants who had served with him twenty and more years ago.

From: *Chem. & Ind.*, 1956, 1420.

ALEXANDER S. RUSSELL

.. 106 ..

Johannes Nicolaus Brønsted

1879-1947



IT IS a difficult task to commemorate and appraise a great man like Brønsted, especially for one thirty years his junior in age, and so much his junior in science. This difficulty is increased by a difference in nationality, and I feel therefore that I ought to begin by acknowledging my debt to the many friends in Denmark who have helped me in the preparation of this lecture. I must mention especially Mrs. Brønsted, who has provided me with much material, especially about Brønsted's early life, and Professor Christiansen, who has made available to me the manuscript of his own memorial lecture to Brønsted. What I have to say owes a very great deal to their willing cooperation.

I shall begin by giving an outline of Brønsted's life and career, followed by some account of his scientific work, and finally I shall try to give a general picture of him as a scientist and as a man.

Johannes Nicolaus Brønsted was born on February 22, 1879, in Varde, a small town in West Jutland. His father was a civil engineer employed by "Hedeselskabet," a corporation founded to reclaim moorland by draining, irrigation, and planting. His mother died shortly after his birth, but his father remarried shortly afterward, and the family moved to a farm in the heart of Jutland, where the young Brønsted and his elder sister spent most of their childhood. This period laid the foundation for the love of country things and country people which played such a great part in his later life. When he was twelve years old his family moved to Aarhus, the second largest city in Denmark, but still an essentially rural environment. He went to school there and seems to have been an apt pupil, particularly in mathematics. There was, of course, no school instruction in chemistry at that time, but Brønsted's interest in the subject was a very early one, his first source of information being an agricultural dictionary which he found in the attic. He did primitive experiments at home in the usual fashion, and the spirit lamp and balance which he used are still in existence.

His father died in 1893, leaving the family in straitened cir-

cumstances. Several friends of the family felt that the young Brønsted ought to begin to earn his living, but his mother recognized his promise and was determined to give him and his sister a good education even if it meant considerable sacrifices. The family moved to Copenhagen, and Brønsted attended the Metropolitan School there, where he found not only a high educational standard, but also a remarkably stimulating set of schoolfellows. Of the twenty boys in his class, two became bishops, two distinguished physicians, and five professors. One of the latter was Niels Bjerrum, his closest friend for many years, and his chief rival in making Danish physical chemistry world-famous. Brønsted matriculated in 1897, and went to study at the Polytechnic Institute in Copenhagen, where he met Charlotte Louise Warberg, whom he married in 1903. His studies seem to have sat lightly on his shoulders, and he found plenty of leisure to cultivate other interests such as philosophy, art, poetry, and music. It was at first intended that he should become an engineer like his father, but after taking his first degree in that subject in 1899 he changed over to pure science, and took his "Magister" degree in chemistry in 1902. At that date this degree was something of a rarity, especially in chemistry, and Brønsted's friends used "Magister" as a nickname for many years afterwards.

There was no academic position immediately available, and Brønsted worked for a short time in an electrotechnical concern. However, he soon returned to the University Chemical Laboratory, and was made an assistant there in 1905. He worked there on his affinity measurements, and in May 1908 presented the third paper in this series (on mixtures of sulfuric acid and water) for his doctorate degree. In the same year a new chair of chemistry was instituted in Copenhagen which combined the duties of teaching physical chemistry to the university students, and inorganic chemistry to students at the Polytechnic Institute. The two competitors for this chair were Brønsted and Niels Bjerrum, who had been Brønsted's classmate at school, and had taken his doctorate degree in the same year. It must have been a very difficult decision for the judges to make; but their choice finally fell on Brønsted; who was appointed at the early age of twenty-nine. The news reached the

Brønsted family in a dramatic way: one day just before Christmas a goods train stopped at the bottom of their garden in the country, and a railway official descended bearing a telegram of congratulation from Bjerrum.

This appointment fixed the whole of Brønsted's subsequent career, as he held the chair until his death thirty-nine years later. His laboratory was at first in the Polytechnic Institute, and for a time facilities were very limited, as physical chemistry was a new subject and the laboratory had to be equipped from scratch. However, conditions gradually improved, and in 1919 he was relieved from the onerous task of teaching elementary inorganic chemistry. The greatest change in his working conditions resulted from his visit to the United States in 1926–27, when he was able to discuss the possibility of financing a new physicochemical laboratory in Copenhagen. The International Education Board finally met the cost of a new University Physicochemical Institute, which was completed in 1930. Here Brønsted had not only ideal working conditions, but also a delightful official residence where he and his family could exercise their hospitality and charm.

I shall now give some account of Brønsted's contributions to physical chemistry, not in strict chronological order, but under their main headings.

The most important general interest in Brønsted's scientific work was undoubtedly thermodynamics. His earlier work dealt entirely with this topic, and even his later work on reaction kinetics has a strong thermodynamic flavor. His series of thirteen experimental papers on "Affinity" appeared during the years 1906–18, and constitute a veritable textbook of thermodynamics. Although Brønsted is well known for his later work on the thermodynamics of dilute electrolyte solutions, it is probably not generally realized how much he contributed to the fundamentals of chemical thermodynamics, where he can be ranked with Nernst and G. N. Lewis. At that time, although it was generally accepted that the affinity of a chemical process was measured by the maximum work and not by the heat of reaction, there were very few accurate or systematic measurements of affinity, and it was this gap which Brønsted set out to fill. In 1906 he showed how the heat and free energy changes in

the interconversion of rhombic and monoclinic sulfur could be measured over a range of temperature, and he also speculated as to how affinity changes could be calculated from purely thermal quantities. It was, of course, Nernst, and not Brønsted, who first solved this last problem successfully, but Nernst himself acknowledged the importance of Brønsted's work in pointing the way. In a later paper in the same series (1910) Brønsted dealt with the thermodynamics of water-sulfuric acid mixtures, and gave one of the first correct treatments of the relations between the various differential and integral thermodynamic quantities in a mixture. In this paper he showed great ingenuity in combining vapor pressure, E.M.F., and calorimetric measurements, and (as in all these early papers) in obtaining accurate results with very modest resources.

Brønsted was always skilled at devising applications of E.M.F. measurements, and one example of this was his measurement of the free energy of formation of naphthalene picrate from its solid constituents, not at first sight a promising system for study by E.M.F. methods. Brønsted pointed out in 1911 that the free energy of this change was measured by the E.M.F. of the cell:

picrate electrode|solution I|H₂Pt, PtH₂|solution II|picrate electrode

where solution I is saturated with picric acid, and solution II with naphthalene + naphthalene picrate. Brønsted suggested using mercury-mercurous picrate for the picrate electrode, but was unable to make measurements on the above cell because the picrate solutions were reduced at the hydrogen electrodes. He was therefore compelled to use a very ingenious but laborious indirect method of measurement. It is interesting to note that in Oxford we have recently been able to measure the E.M.F. of the cell originally proposed by Brønsted by replacing the hydrogen electrodes by glass ones (which of course were not available to him): the value obtained for the free energy of formation is exactly the same as that obtained in 1911 by the indirect method (Bell and Fendley, *Trans. Faraday Soc.*, 1949, 45, 121).

Brønsted's thermodynamic studies soon led him into the field of electrolytes, first through E.M.F. measurements, and later through

studies of solubility. It was becoming clear, partly through the work of Bjerrum, that very many electrolytes were completely dissociated in solution, and that their deviations from ideal thermodynamic behavior could not be explained in terms of any association equilibrium. The concept of "activity" had been introduced by G. N. Lewis, and various authors had suggested that electrostatic forces between the ions might be of importance. Brønsted's approach was essentially an experimental one, and his solubility measurements became famous in 1924, when with LaMer he published data on activity coefficients of ions in very dilute salt solutions which provided a most striking confirmation of the theoretical treatment of Debye and Hückel, published while the work was in progress. It should, however, be stressed that this publication with LaMer was really the fifth of a series of papers on solubility, starting in 1919, interspersed with a number of other papers on the properties of ionic solutions. It is in fact remarkable how many important laws Brønsted was able to discover on the basis of his carefully designed and accurate experiments, in most cases before any theoretical basis for these laws was available. Thus he was able to show that the deviations of ionic solutions from ideal behavior increase greatly with an increase in the charges on the ions present, and that in a solution containing several electrolytes the thermodynamic behavior of a given ion is mainly a function of the ionic strength μ , defined as

$$\mu = \frac{1}{2} \sum m_i z_i^2,$$

where m_i is the concentration of an ion of charge z_i , and the summation extends over all the ions in the solution. In more concentrated solutions ions show individual properties not depending only on their charge, and Brønsted's "Principle of the Specific Interaction of Ions" (1921) states that the individual properties of a given ion depend mainly on the ions of opposite charge which are present in solution. Brønsted's investigations on the effect of salts of ionic equilibria will be described under his kinetic work, but one simple principle is worth mentioning here: that even an ionic equilibrium will obey the classical law of mass action in presence of a large excess of nonparticipating salt. All these principles were later shown to have theoretical bases, and if we add to Brønsted's work

the equally important investigations of his countryman Bjerrum, it will be seen that Denmark has had an altogether disproportionate share in the experimental foundations of the modern theory of electrolytes.

Most of Brønsted's solubility determinations, and many of his other researches, were carried out with the cobaltammines. These had been studied in great detail from the preparative point of view by S. M. Jørgensen, Brønsted's teacher, and he therefore had to hand large numbers of specimens and much information about these compounds. This was naturally a piece of good fortune, but Brønsted's genius lay in realizing how admirably suited they were for his purposes. By suitable variations in the nature of the six groups coordinated to the central atom, ions can be produced with valencies varying from $+3$ to -3 , and by combining these ions with one another or with other anions or cations it is possible to obtain salts of many charge types and of widely varying solubility. Most of these salts are well defined and crystalline, and they can be determined accurately even in very dilute solution by the simple process of treatment with sodium hydroxide and distillation of the ammonia into standard acid. These properties made them almost ideal for investigation of solubilities in salt solutions, but there was a great deal of groundwork to be done before the most suitable salts could be chosen: thus in his 1920 paper he measured the solubilities of 90 salts at two temperatures. The salts finally used by Brønsted and LaMer were the following:

$[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]^-$	$s = 4.9 \times 10^{-4}$
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)(\text{CNS})]^+[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]^-$	$s = 3.3 \times 10^{-4}$
$[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]_2^+[\text{S}_2\text{O}_6]^-$	$s = 1.5 \times 10^{-4}$
$[\text{Co}(\text{NH}_3)_6]^{+++}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]_3^-$	$s = 5.0 \times 10^{-4}$

The saturated solutions were obtained by the simple expedient of letting the solvent trickle slowly down a long vertical tube packed with crystals, a method which had been used by Brønsted much earlier in his measurements on rhombic and monoclinic sulfur. In spite of the low solubilities involved, an accuracy of about 0.3% was attained. . .

The cobaltammines also played a considerable part in the development of Brønsted's ideas on acids and bases, and there is one

other example of their use which may be mentioned here. On a simple electrostatic picture the solubility of a salt in different solvents should be a smooth function of the dielectric constant, but this is not so in practice, no doubt largely because of the part played by nonelectrostatic factors. In a paper given to the 1931 meeting of the British Association Brønsted reported solubility measurements on the two substances $\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3$ and $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$ which contain exactly the same chemical groupings, but are respectively a nonelectrolyte and a uniunivalent salt. By considering the ratio of the solubilities of these two substances, rather than the solubility itself, he hoped to eliminate the nonelectrostatic factors, and he did in fact find a fairly regular behavior for nine solvents with dielectric constants ranging from 21 to 84.

Apart from electrolytes, a particular thermodynamic problem which interested Brønsted from 1930 onward is the effect of molecular size on thermodynamic properties. He carried out experiments on the solubilities and distribution between phases of molecules (or colloidal particles) which were chemically very similar, and differed mainly in size. These led him to the concept of an "isochemical series," and he established several laws governing the solubilities and other properties of such a series. Although he did not realize that large entropy effects might be present in mixtures of molecules of different sizes, Brønsted's laws are essentially the same as those developed recently for high polymers such as rubber. Some of Brønsted's last published work was on the vapor pressures of mixtures of the normal paraffins, for which he obtained experimental results of very high accuracy, and established some new regularities which have not yet been explained theoretically. This work contains some very neat experimental devices: for example, in order to weigh a vessel containing liquid and vapor without detaching it from the rest of the apparatus, he suspended it from an ordinary balance and used as a connecting tube such a fine glass capillary that it had little effect within the sensitivity of the balance.

Brønsted's work on isochemical series is of particular interest, because it represents one of the few cases in which he gave a

molecular interpretation for the laws which he had established experimentally. In general he was curiously reluctant to consider any detailed molecular picture, preferring to derive from experiment empirical regularities which should be independent of any particular features of the molecules concerned. For example, one sometimes felt that he regretted the mechanistic explanation given by the Debye-Hückel theory for the laws which he had established experimentally, and other examples of a similar attitude will be given later. I well remember his indignation when I suggested to him, shortly before his death, that a statistical approach was helpful in explaining the laws of thermodynamics to students.

Certainly there was no suggestion of any molecular interpretation in his writings on the fundamental bases of thermodynamics, which occupied him to an increasing extent during the last ten years of his life. Although he criticized severely the conventional approach to the second law, his treatment remained a strictly phenomenological one. It is difficult to give an estimate of the value of this work, and I shall not attempt to summarize its content here. It roused violent controversy in Denmark, but has received little attention elsewhere: it is usually regarded as formally correct, but rather sterile. It is true that a similar view was at one time held about Brønsted's acid-base definition, which proved to have such a widespread importance, and it would indeed be interesting if his concepts of heat and entropy should eventually prove equally fruitful. They may perhaps be helpful in treating processes in which a steady state is set up by the irreversible flow of energy or matter through the system, a field which Brønsted had begun to study experimentally shortly before his death.

The second main field of Brønsted's activities was reaction kinetics, and in particular catalysis by acids and bases. This interest arose comparatively later in Brønsted's scientific development, but is probably the work for which he is best known, especially outside Denmark. It was closely connected with his work on electrolytes, and it is difficult to trace the exact order in which the various interwoven ideas arose, since papers on both kinetic and thermodynamic topics followed one another with bewildering rapidity in the nineteen-twenties.

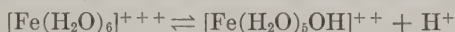
Brønsted first used kinetic measurements in 1921 in connection with the effect of salts on acid-base equilibria. He was particularly concerned to show that the effect of salt concentration on hydrogen-ion concentration depends on the nature of the equilibrium involved: for example, in the system



the hydrogen-ion concentration will be increased by added salt, while the equilibrium



will be little affected by salt additions, and in the system



the hydrogen-ion concentration will be decreased by addition of salt. These results follow directly from the Debye-Hückel expression for activity coefficients, but were derived by Brønsted from the experimental evidence on the activity coefficients of ions of different charges. In order to test his conclusions it was necessary to measure the hydrogen-ion concentrations in these solutions, and for this purpose he used the rate of reaction of diazoacetic ester with water to give glycolic ester and nitrogen, a well-known example of hydrogen-ion catalysis. This at once raised questions of fundamental importance, for it was held in many quarters that the reaction velocity in such a system was proportional to the activity rather than to the concentration of hydrogen ions. Brønsted showed definitely that the concentration was the appropriate quantity: for example, when only a strong acid is present, the effect of added salt on the reaction velocity is much less than its effect on the hydrogen-ion activity. This justified the use of the diazoacetic ester reaction for measuring hydrogen-ion concentrations, and the salt effects observed with solutions of weak electrolytes agree with those predicted from activity data. This type of kinetic salt effect, depending on the displacement of an equilibrium, was termed by Brønsted a "secondary salt effect."

There existed at the time a mass of uncoordinated data on the effect of added salts on reaction velocities, including many reactions involving only strong electrolytes, where no secondary salt effect could be involved. In this latter class of reaction it is customary to speak of "primary salt effects." Brønsted next showed

in 1922 that all the existing data for primary salt effects could be summarized by the following simple statement: reactions between ions of like charge exhibit a large positive salt effect, reactions between ions of unlike charge a large negative salt effect, and reactions between an ion and a neutral molecule a small salt effect which may be either positive or negative. This classification was in itself a great step forward, but Brønsted gave it a further interpretation in terms of his famous expression for the effect of environment on the rate of chemical reaction. For a reaction between two species A and B the expression for the reaction velocity v is

$$v = k[A][B] \frac{f_A f_B}{f_X} \dots \dots \dots (1)$$

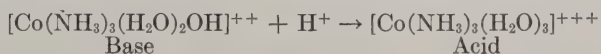
where k is independent of environment, f is an activity coefficient, and X represents the "critical complex" of A and B through which they must pass in order to react. It now seems obvious to us that the correct expression must involve the activity coefficient of some intermediate complex, as well as those of the reacting species, but Brønsted was the first to realize this, although the concept of a critical complex had previously been employed by Marcellin. We know very little about the nature of X, but we do know that its charge is the algebraic sum of the charges on A and B, and this is sufficient to predict approximately how its activity coefficient will vary with salt concentration. Nowadays this prediction would be made on the basis of the Debye-Hückel theory, but Brønsted again had to use the experimental data available for ionic activity coefficients, and was able to show that equation (1) corresponds to the rules for the salt effect given above, and agrees approximately with the magnitude of the observed effects. In particular it shows that in a reaction involving an ion and a neutral molecule (such as the decomposition of diazoacetic ester ion in presence of hydrogen ions) the activity coefficient factor will be near to unity, and hence the reaction velocity will be proportional to the concentrations of ester and hydrogen ions, and not to their activities. After the advent of the Debye-Hückel theory, Brønsted made more measurements on salt effects in very dilute solutions, and found a complete confirmation of equation (1). It is interesting to note that Brønsted did not attempt to give any detailed molecular explanation of this equation, and the semithermodynamic derivation which he gave in

1922 was not made much clearer by a more detailed treatment in 1925. Brønsted's equation is now of course regarded as a special case of the transition-state expression for reaction velocity, but Brønsted himself showed little interest in later developments in this field.

The second major advance which served to clarify a large mass of kinetic work was Brønsted's extended definition of acids and bases, first published in 1923. Identically the same definition was put forward almost simultaneously by Lowry in this country. This definition is now generally accepted: it states that *an acid is a species which has a tendency to split off a proton, and a base is a species which has a tendency to add on a proton*. All acids and bases can therefore be arranged in conjugate or corresponding pairs according to the scheme



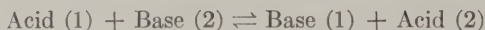
This definition of acids includes not only uncharged molecules such as $CH_3 \cdot CO_2H$, but also anions like HSO_4^- , $HPO_4^{=}$ and cations like NH_4^+ , $[Fe(H_2O)_6]^{+++}$. The new definition of bases was even more fruitful, since there had previously been great confusion, for example, as to whether the ammonia molecule or the hypothetical ammonium hydroxide should be regarded as a true base. The Brønsted-Lowry definition includes unchanged bases like NH_3 , NMe_3 and anion bases such as $CH_3 \cdot CO \cdot O^-$, OH^- , $CO_3^{=}$. It was not so easy to find an example of a cation base, but once again the cobaltammines and similar compounds came to the rescue: for example, the ion $[Co(NH_3)_3(H_2O)_2OH]^{++}$ is a base in virtue of the reaction



It is immediately clear that the hydroxyl ion is not in any way unique, since it is only one member of a whole class of anion bases. On the other hand the hydrogen ion does appear to occupy a privileged position as long as we write it as H^+ , i.e., a bare proton. However, following Fajans and others, Brønsted realized that the free proton could not exist in any significant concentration in the presence of other molecules, and that in aqueous solution it existed as the hydroxonium ion, H_3O^+ , entirely analogous to the ammonium ion, NH_4^+ . In fact, the "hydrogen ion" is a different

entity in each solvent, in each case being only one of a class of cation bases.

Once the claim of hydrogen and hydroxyl ions to uniqueness has been abandoned, it becomes possible to write all the reactions of acids and bases (variously described as dissociations, neutralizations, hydrolyses, buffer systems, etc.) in the symmetrical form:



Some examples of this are given in the following table, and a similar set could be given for nonaqueous solvents.

A_1	+	B_2	\rightleftharpoons	A_2	+	B_1	Description.
$\text{CH}_3 \cdot \text{CO}_2\text{H}$		H_2O		H_3O^+		$\text{CH}_3 \cdot \text{CO} \cdot \text{O}^-$	Dissociation in water <i>or</i> buffer action in acetic acid + acetate.
$\text{CH}_3 \cdot \text{CO}_2\text{H}$		NH_3		NH_4^+		$\text{CH}_3 \cdot \text{CO} \cdot \text{O}^-$	Dissociation of acetic acid in liquid ammonia, <i>or</i> dissociation of ammonia in glacial acetic acid, <i>or</i> neutralization of $\text{CH}_3 \cdot \text{CO}_2\text{H}$ by NH_3 , with or without solvent.
H_2O		$\text{CH}_3 \cdot \text{CO} \cdot \text{O}^-$		$\text{CH}_3 \cdot \text{CO}_2\text{H}$		OH^-	Hydrolysis of acetate solutions.
NH_4^+		H_2O		H_3O^+		NH_3	Hydrolysis of ammonium salts, <i>or</i> buffer action in $\text{NH}_3 + \text{NH}_4\text{Cl}$.
H_2O		HPO_4^-		H_2PO_4^-		OH^-	Hydrolysis of secondary phosphates.
H_2O		NH_3		NH_4^+		OH^-	Dissociation of ammonia in water.
H_2PO_4^-		H_2O		H_3O^+		HPO_4^-	Dissociation of primary phosphate <i>or</i> buffer action in mixtures of primary and secondary phosphate.

Since the hydrogen and hydroxyl ions are not unique among acids and bases, there is no reason why they should have the monopoly of catalytic action in chemical reactions, and Brønsted's next important contribution was the experimental demonstration of *general acid-base catalysis* in a number of reactions. Brønsted and Pedersen's paper on the nitroamide decomposition, published in 1924, showed that the reaction was catalyzed by the following classes of base:

- (1) Anion bases like acetate ion, oxalate ion, etc.
- (2) Uncharged bases like aniline and pyridine.
- (3) Cation bases like $[\text{Co}(\text{NH}_3)_5\text{OH}]^{++}$.

Brønsted and Pedersen made a detailed study of catalysis by anion bases, and later papers (1925–34) extended this to the other types of base and also to nonaqueous solvents. The mutarotation of glucose offered rather more complications, since it is catalyzed by both acids and bases. Thus, in an acetate buffer solution the full expression for the reaction velocity is

$$v = k_0 + k_1[\text{H}_3\text{O}^+] + k_2[\text{OH}^-] + k_3[\text{HOAc}] + k_4[\text{OAc}^-]$$

However, by carefully designed experiments it was possible to separate the effects of different species, and the 1927 paper by Brønsted and Guggenheim demonstrated the catalytic effect of anion bases, uncharged bases, cation bases, uncharged acids like acetic acid, and cation acids like the ammonium ion. Very similar conclusions were published by Lowry in the same year, although his investigations were less complete.

The idea of catalysis by species other than hydrogen and hydroxyl ions was not altogether a new one, and in particular the "dual theory," suggested by Acree, Snothlage, and H. S. Taylor, had assumed catalysis by undissociated acid molecules. However, most of their deductions were based upon incorrect values for the degree of dissociation of electrolytes, and did not allow for primary and secondary salt effects. In his monograph on "acid-base catalysis" (published in Danish in 1926, English translation in 1928) Brønsted devoted a good deal of space to a severe criticism of this earlier work, and was in fact able to show that in almost all cases the supposed catalytic effect of acid molecules was based on a misinterpretation of the data, or could reasonably be attributed to a salt effect. The only notable exception to this statement was Dawson's work on the acetone-iodine reaction, and here Brønsted's strictures were rather less than just. It is true that Dawson did not take into account recent views on electrolytes and that his experiments were planned in such a way as to involve complicated salt effects. Nevertheless, there is no doubt that his work definitely establishes catalysis by carboxylic acid molecules, and in fact still provides the most extensive set of data for this type of catalyst, although his numerical values need some revision in the light of modern developments.

If we consider a series of similar acids and bases, it is natural

to expect that their catalytic power for a given reaction will depend on their acidic or basic strength. In his first paper on the nitroamide decomposition Brønsted gave a quantitative form for this dependence which has been found to be generally valid, and which is commonly known as the "Brønsted relation." For basic catalysis it can be written in the form:

$$k_b = GK_b^\alpha$$

where k_b is the catalytic coefficient of a base of dissociation constant K_b , and G and α are constants characteristic of the reaction, the temperature, and the solvent, α being less than unity. . . . As in many other cases Brønsted arrived at the form of this relation primarily by considering the experimental data. The only theoretical basis which he gave for it was a vague and unsatisfactory one, and he was not particularly interested in later attempts to interpret the relation in terms of molecular potential-energy curves.

I must now attempt some kind of summing up of Brønsted as a scientist and as a man. His skill as an experimentalist was not immediately apparent because of the simple nature of many of his methods, and it took some time to realize how much skill and discrimination lay behind an apparently simple piece of experimental work. His great strength lay in the choice of the most suitable substance or reaction, and in the planning of a series of experiments to attain the desired end with the greatest certainty and economy. For this reason his researches always had a much wider application than the immediate purpose in hand, and one of the greatest benefits of working with him was the opportunity of sharing his insight into general methods and planning of research. Many of his pupils have modeled their subsequent work on Brønsted's prototypes: for example, most later work on activity coefficients from solubility measurements and on general acid-base catalysis follows closely on some lead originally given by Brønsted.

It is more difficult to place Brønsted as a theoretical physical chemist in relation to the main developments of his time. We have already seen several examples of his absorption in thermodynamics and his love of an experimental approach, and the adjective "classical" seems an appropriate one to describe his contributions to physical chemistry. In the field of solutions his work has had a

clarifying effect to which it is difficult to find a parallel. Although his mind was a most agile one, several of the major trends in modern physical chemistry failed to rouse his interest: for example, the experimental and theoretical study of molecular structure, and the theoretical treatment of reaction velocities. Looking back, it seems strange that one of the greatest investigators of reaction kinetics in solution should never have deliberately measured an activation energy. On the other hand, there is no doubt that this limitation of interest enabled him to attack his chosen field with greater intensity and singleness of vision.

Brønsted was an individualist in his work, and owed little to the influence of other scientists, although the tradition of Julius Thomsen fostered his early interest in thermodynamics, and his training under S. M. Jørgensen introduced him to the cobaltamines and gave him high standards of preparative and quantitative work. There is only one instance where he collaborated with another scientist outside his own field, and that was in his famous work with Hevesy on the separation of the isotopes of mercury and chlorine by ideal distillation at low pressures. In his earlier days he had few junior collaborators, but in the period 1922–37 many chemists from other countries, particularly England and the United States, went to work with him. I myself spent four years in his laboratory, and I remember very clearly the impression of integrity and intensity of scientific endeavor which I received. One guest worker described his laboratory as a place of “high chemical potential,” and the phrase does give something of the tense and personal feeling which Brønsted inspired. He showed great kindness and consideration to his collaborators from overseas, and the subsequent work done by many of them shows the lasting effect of his influence. On first acquaintance he seemed rather reserved, but one soon realized that this arose from an unwillingness to talk carelessly or lightly on scientific matters. When he had once embarked on a discussion his acuteness and remorseless logic were remarkable, and there can be very few occasions on which he was worsted in a scientific argument. He did in fact very much enjoy a keen polemical discussion, and never hesitated to express his criticisms in an edged and sometimes personal manner. This in-

volved him in a number of controversies, beginning in 1908 with his criticism of Nernst's concept of "ideal concentrated solutions," and ending with a lengthy argument with Danish physicists about the foundations of thermodynamics.

Brønsted's duties as a professor involved a considerable amount of elementary teaching, especially in his earlier days, and his lectures were elegant in delivery and content. Their concentrated exactness made them perhaps rather indigestible for the average student, and the same was true of his textbook of physical chemistry. The later editions of this book incorporated his own treatment of thermodynamic principles, and we can sympathize with the polytechnic student who had to use terms like "heat" and "work" in one sense in his physics and engineering, and in another sense in his chemistry. The Danish system involves a large amount of oral examination, and in his earlier days Brønsted gained some reputation for severity as an examiner: his standards were certainly high, and he was not much given to compromise, least of all in scientific matters. There are many anecdotes about these examinations, and I remember one candidate who had rashly professed some knowledge of the occurrence and properties of the silicates, and who was finally driven by Brønsted's remorseless logic into maintaining that a paving stone would probably dissolve completely if stirred up with a little water! However, as he became older Brønsted became more lenient toward his younger students, although he could still be a formidable opponent to candidates for the doctorate degree.

In private life Brønsted had great personal charm and a wealth of interests outside his science. The chief of those was his love of the countryside and its people, which remained with him all his life. His family holidays were usually spent in some remote part of the country, and he had a very extensive knowledge of Danish wild life, especially of birds. It is interesting to note that his last publication, just before his death, was a note describing some observations on insect behavior made during his summer holiday. He felt very keenly about the preservation of natural beauty and nature reserves, and took a prominent part in campaigns to this end. Music and painting were also among his accomplishments, and through

his marriage he came into close contact with many of Denmark's leading artists and musicians. He had a wide knowledge of literature in several languages and a remarkable gift not only for accuracy but also for elegance in expression in both Danish and English.

Brønsted traveled widely in Europe, and made several visits to the United States. In spite of his strong Danish patriotism he had a great deal of sympathy and understanding for other countries, and especially for England. His early contacts were mostly with German scientists, but after the First World War his sympathies turned decisively toward this country. In 1920 he spent several months in England, mainly with Professor Donnan at University College, and he made at least seven more visits before 1939, including several to attend meetings of the Faraday Society. Among many other honors he was made an honorary member of the Academy of Arts and Sciences in 1929, an honorary fellow of the Chemical Society in 1935, and an honorary doctor of London University in 1947.

The Second World War served only to strengthen the ties which bound him to English things and English people, and he never had any doubts as to the rightness or the eventual outcome of the struggle. From the first day of the German occupation he spent several hours daily listening to the broadcast news from London, and he also read widely in English history and biography: when I visited him in 1945 he still had on his table a list of English Foreign Secretaries from 1769 onward. The occupation also turned his attention to public affairs in general, in particular the vexed question of Schleswig and the Danish-German frontier, about which he spoke and wrote in his usual forthright manner. Nevertheless, it was a surprise to many of his friends when in 1947 he accepted nomination as a candidate for the Danish parliament, and a still greater one when on October 28 he was elected. He took this responsibility seriously, and immediately began to study parliamentary procedure, but he was overtaken by his last fatal illness before he could take his seat, and died on December 17. It is interesting to speculate how he would have fared in Parliament and how his logical and uncompromising mind would have dealt with the half-truths of politics. He himself believed that many of the ills of mankind were due to the lack of logic and precise definition in

public affairs, and it is an open question whether the application of this principle would have brought success or frustration.

The Brønsted Memorial Lecture, delivered before the Chemical Society in London, Feb. 3, 1949. Selections from *J. Chem. Soc.*, 1950, 408.

RONALD PERCY BELL

.. 107 ..

Niels Janniksen Bjerrum

1879-1958



NIELS JANNIKSEN BJERRUM was born on March 11th, 1879, the son of the well-known eye-specialist and professor of ophthalmology Jannik Petersen Bjerrum (born 1851, died 1920) and his wife Anna Katrine Lorentine Johansen (born 1856, died 1941). Both his father and his mother came of families of North Schleswig farmers. He can trace his descent through eight generations, with the names Niels, Jannik, and Peder alternating, back to Peder Nielsen Bierum born on October 12th, 1635. Niels was the eldest of eight children. Bjerrum's paternal aunt Dr. Kirstine Meyer, a distinguished physicist, lived in their home from 1880 to 1885 and was like a second mother to him. She undoubtedly stimulated his interest in the physical sciences.

During Bjerrum's childhood and youth, frequent and numerous visitors to his home included well-known professional men, especially doctors, scientists, and politicians. On Sunday evenings their house was open to all their intimate friends and there would often be a full score of guests for dinner. Thus did young Niels grow up in a happy, liberal, intelligent, and tolerant milieu throughout the period when his character was developing.

Niels spent all his summer holidays at the home of his maternal grandfather in Kolding in Jutland. Here he acquired at an early age his lifelong love of the countryside and more especially of the sea. His grandfather was a cabinetmaker, and Niels when a small boy learnt to use carpentry tools which he applied especially to making model ships of gradually increasing complexity.

Niels began to go to school at the age of five. Between the ages of twelve and eighteen he was at the Metropolitan School. He had several outstanding schoolfellows, including J. N. Brønsted who remained for many years his friendly rival. Niels found mathematics and natural history easy, but languages difficult. However, he passed the university entrance examination with overall high marks to the pleasant surprise of his languages teacher.

On leaving school in the summer of 1897 Bjerrum was still undecided whether he wanted to read chemistry or mathematics, but

in the end he chose chemistry and in February, 1898 he began a university course lasting four years. His teachers included Professor Jørgensen, the contemporary and rival of Werner in the field of metal complexes.

In January, 1902 Bjerrum obtained his master's degree for which he was required to submit a thesis entitled "A critical-historical survey of the isomerism of fumaric and maleic acid." His examiner, Professor Jørgensen, nearly failed him because the candidate had the temerity to extend his criticism to the chemistry instead of confining it to the history!

The very same month by good fortune a post of assistant at the University Chemical Laboratory fell vacant. Bjerrum applied for this post and was appointed at a commencing salary of 1000 Kr. (about £50) per annum with some small extras. However, this gradually increased so that by the time he married in 1907 he was earning about 3000 Kr. per annum.

Bjerrum's enthusiasm for research received no encouragement from his seniors. In August, 1902 Professor Martin Knudsen put him on to the thrilling problem of investigating the accuracy of the determination of chloride in sea water. He published a couple of papers on this subject but was glad to drop it and work on something more interesting. Bjerrum had learnt from Jørgensen many of the experimental facts, if not much theory, concerning complexes and had been struck by certain parallels between green chromium chloride and cobaltammine salts. He accordingly chose for his research the field of chromic compounds which kept him actively occupied and interested for the next six or seven years.

In the summer of 1905 Bjerrum spent three months in the Institute of Physical Chemistry in Leipzig of which Ostwald was still nominally director but Luther was in active control. Here Bjerrum met and became friendly with Luther, Bodenstein, von Halban, Drucker, and C. Benedicks. It was during this visit that Bjerrum published his famous paper containing a theoretical and experimental study of the use of a bridge of concentrated potassium chloride to reduce the overall liquid-liquid junction potentials. It is unfortunate that the title of this paper contained the word "elimination" instead of "reduction" because subsequent history indi-

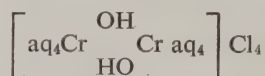
cates that many people read the title but few read the text of this valuable paper.

When Bjerrum began his research on chromic compounds, salts of the bluish-violet $[\text{Cr}, \text{aq}_6]^{3+}$ and of the green $[\text{CrCl}_2, \text{aq}_4]^+$ were well known. Bjerrum studied the hydrolysis of green $[\text{CrCl}_2, \text{aq}_4]\text{Cl}$ to violet $[\text{Cr}, \text{aq}_6]\text{Cl}_3$ and came to the conclusion that the ion $[\text{CrCl}, \text{aq}_5]^{2+}$ was formed as a relatively unstable intermediate. He succeeded in isolating green salts containing this ion, in particular the chloride and sulphate. He proved that the sulphate $[\text{CrCl}, \text{aq}_5]\text{SO}_4$ was identical with a compound previously prepared by Recoura and erroneously supposed by Werner to have the structure of the double salt $[\text{Cr}, \text{aq}_6][\text{CrCl}_2, \text{aq}_4][\text{SO}_4]_2$ which had been obtained both by Werner and Huber and independently by Weiland and Krebs. All this may seem to be rather ordinary inorganic chemistry of interest only to specialists in the chemistry of chromium. In fact this work was a striking example of the application of physical chemistry to a problem of inorganic chemistry. Bjerrum gave three independent proofs of the constitution of Recoura's compound. The first was from conductance measurements. The second was based on rates of hydrolysis. The third was based on extinction coefficients. A paper, 122 pages long, entitled "Studies on chromic chloride" was published by the Royal Danish Academy in 1906 and awarded their silver medal which had been awarded to only three other chemists over the previous twenty years.

In the spring of 1907 Bjerrum married Ellen, the beautiful and lively daughter of Peter Dreyer a wine-importer in Randers. The same summer he again visited Germany and, what is more important, went to Zürich to see Werner. He told Werner about his research on Recoura's compound $[\text{CrCl}, \text{aq}_5]\text{SO}_4$. Contrary to the forebodings of Professor Emil Petersen, Bjerrum's chief, Werner, was interested and recognized that Bjerrum's conclusions were right while his own earlier interpretation was wrong.

In the continuation of this work Bjerrum's interest was directed especially to basic chromic compounds obtained by hydrolysis of salts of the bluish-violet ion $[\text{Cr}, \text{aq}_6]^{3+}$. He showed that there are two distinct types which he called "manifestly basic" and "latently basic." Typical of the former class are the soluble green

$[\text{CrOH}, \text{aq}_5]\text{Cl}_2$ and $[\text{Cr}(\text{OH})_2, \text{aq}_4]\text{Cl}$ and the grey-green insoluble $[\text{Cr}(\text{OH})_3, \text{aq}_3]$. Equilibrium between these is established rapidly and is determined by the acidity of the solution. Bjerrum showed that "even in rather involved cases the law of mass action in combination with the theory of electrolytic dissociation gives a correct evaluation of the factors governing hydrolysis when one confines oneself to the investigation of dilute solutions." Bjerrum determined the several equilibrium constants at two or three temperatures and derived values for the heats of reaction. The "latently basic" compounds, also green, are easily soluble in water, contain no Cl bound in the complex, react slowly with acid and contain more than one chromium atom per ion, e.g.,



an early example of what is now called hydroxyl bridging. The physical chemistry of these compounds is complicated and, although this early work of Bjerrum was continued in collaboration with Faurholt over the years 1924 to 1927 there is still much to be learnt about them. They apparently play an important part in tanning. This work was published in 1908 as a thesis which earned Bjerrum the degree of Doctor of Philosophy in the University of Copenhagen (awarded only for completely independent unaided work and thus only distantly related to Anglo-Saxon Ph.D. degrees). The detailed results of this research are of rather specialized interest, but the physicochemical methods used were revolutionary (in the best sense of the word). The study of complex compounds had hitherto been mainly restricted to preparation and identification. Reagents were mixed and precipitates recrystallized. The chemical reactions of the purified compound were studied, but usually the only physicochemical measurement was that of conductance. Bjerrum introduced several new methods of study. He used the hydrogen electrode to determine equilibrium constants some years before Sørensen had introduced the term pH. He made such measurements at several temperatures and used thermodynamics to derive heats of reaction. Instead of merely recording visual observation of colour he made quantitative determinations of absorption spectra and drew quantitative conclusions

concerning the concentrations of molecular or ionic species in solution. Not only were the techniques new, so was the point of view. Bjerrum was not satisfied with qualitative conclusions concerning the products of some process. He set out to determine the several species present in solution, their respective amounts, their rates of transformation into one another, and the equilibria between them. It is not surprising that Werner was favourably impressed. What is most surprising is that Bjerrum must have learnt physical chemistry almost entirely by independent reading of Ostwald's books. There was certainly no professor in Copenhagen who could have taught him these methods of approach, with the possible exception of Julius Thomsen—but Thomsen gave only first-year lectures and had retired before Bjerrum graduated.

This work set the pattern for all subsequent quantitative research on complexes. First and foremost must be mentioned Bjerrum's own comprehensive work, begun in 1909 and published in 1915, on the whole family of thiocyanatochromium compounds $\text{Cr}(\text{CNS})_n, \text{aq}_{6-n}$ where n has all values between 1 and 6. Of especial interest is the nonelectrolyte ($n = 3$) coming between the cations ($n < 3$) and the anions ($n > 3$). Bjerrum succeeded in proving the existence of all six thiocyanatochromic complexes, isolating four of them and finding analytical methods for determining the amounts of all six. He determined the six equilibrium constants at 50° and the rate constants of interconversion at 17° . This work was rewarded with the rarely bestowed gold medal of the Royal Danish Academy: during the first half of the present century the gold medal was awarded to only two other scientists, a geologist and a physicist. Also worthy of mention is analogous work by Bjerrum with the collaboration of Kirschner on thiocyanatoaurous and thiocyanatoauric compounds published in 1918. It is interesting that as late as 1947 Bjerrum published work of a similar kind on equilibria involving chloroauric and chloroaurous compounds. Last, but not least, must be mentioned that in the wide field of quantitative work on the stability constants of all kinds of complexes one of the world's leading authorities is Niels Bjerrum's son and pupil Jannik Bjerrum.

In 1907 both the chemistry chairs in the University of Copenhagen fell vacant. They were filled by Biilmann, the organic chem-

ist, and by Julius Petersen, the inorganic chemist. Neither chair was likely to fall vacant again for many years. A third chair was created in 1908. It is not altogether clear to what extent its first holder had to be a physical chemist. Anyhow the two candidates for the chair were Bjerrum and Brønsted. Both were exceptionally outstanding physical chemists and either in the absence of the other would have had a walk-over. It was decided that the two candidates should compete by delivering five lectures, three on a subject chosen by the candidate and two on a set subject. Bjerrum chose "Colour and structure of electrolytes," *i.e.*, the subject of his own research work; Brønsted chose "Gaseous equilibria," a subject of classical thermodynamics. Bjerrum was at a disadvantage because his public defence of his thesis, which is the final stage of obtaining the doctor's degree, took place only a week before the beginning of the competition whereas Brønsted had completed the formalities for his doctor's degree some months earlier. The selection committee, contrary to custom, issued a public statement praising both candidates but voted unanimously for Brønsted. If the candidates had been judged on their research work it is an open question who would have won. But they were in fact judged on their ability as lecturers. Brønsted had a natural gift for public speaking. Bjerrum always found it an effort. This defeat was a hard blow for Bjerrum who was honestly convinced that he was the better physical chemist. It was also a depressing thought that no other chair was likely to be vacant for many years. However, he soon recovered his good spirits and the next half dozen years were in many ways the most active and productive years of his career.

In 1909 Bjerrum attended the Seventh International Congress of Applied Chemistry in London and presented a paper entitled "A new form for the electrolytic dissociation theory." In his work on chromic salts he had shown that, whereas salts containing the ions $[\text{Cr}, \text{aq}_6]^{3+}$, $[\text{CrCl}, \text{aq}_5]^{2+}$, and $[\text{CrCl}_2, \text{aq}_4]^+$ have distinct absorption spectra, the absorption of light per chromium atom in salts containing $[\text{Cr}, \text{aq}_6]^{3+}$ is constant over a five-fold range of concentration and nearly constant over a twenty-five-fold range of concentration, and is identical for chloride, nitrate, and sulphate. At first Bjerrum interpreted this to mean that ionization had no effect

on colour, but he gradually became aware of the much more reasonable explanation which he expounded in the above-mentioned paper. In this paper Bjerrum wrote, "These colour-relations found in connection with electrolytic dissociation can best be explained by changing Arrhenius's hypothesis in the following manner: We suppose that the strong electrolytes always are completely separated into ions, and that this is the reason why they always have the same colour in all concentrations. If changes of colour take place in solutions of an electrolyte, the ions have more or less entered into combination with each other, the dissociation is not complete. If this hypothesis is correct, then the decrease in molecular conductivity and in molecular depression of the freezing-point that accompanies the increase in concentration must be due to the action of the electric charges of the ions on each other." "It accords well with this new form for the dissociation theory that the 'degree of dissociation' which has been calculated from the molecular conductivity is, in the case of strong electrolytes, approximately determined by the valency of the ions (Ostwald-Walden's rule), by the dielectric constant of the solvent (Walden), and by the concentration of the salt. The fact that the so-called 'degree of dissociation' depends upon the electric constants of the substances without admitting of any specific influence by chemical affinity becomes quite natural when this quantity in reality is the decrease in electrolytic friction due to the electric forces among the ions. And the fact that the law of mass action does not apply to the influence of the concentration on the degree of dissociation of strong electrolytes will no longer be an inexplicable anomaly." Arrhenius was present at the meeting. He regarded Bjerrum's modification of his theory of ionic dissociation as a personal affront which he refused even to discuss with Bjerrum. Walden and Donnan, who were also present, were among the first to take the new theory seriously. It is interesting that G. N. Lewis at the same period observed that the additivity of properties of electrolyte solutions pointed to complete dissociation but was unwilling to accept this interpretation. He wrote:¹ "If we had no other criterion for the degree of dissociation, these facts would undoubtedly lead us to regard salts, up to a concentration of normal or half normal as completely dissociated . . .

I believe that we shall make no great error in assuming that the degree of dissociation calculated from the conductivities is in most cases substantially correct."

Bjerrum wrote nothing further on this subject until 1916 when he presented a paper at a Congress in Christiania in which he marshalled the evidence in favour of complete dissociation. He recalled the evidence from optical properties and the fact that the thermodynamic properties of electrolyte solutions are determined mainly by the concentration and electric type. In 1912 Milner had developed the first sound, though only approximate, theory of the effect on the thermodynamic properties of the Coulomb interaction between the ions. Bjerrum showed that freezing points could be explained at least semiquantitatively by this Milner effect without any need for assuming incomplete dissociation, but it was impossible to obtain agreement by assuming incomplete dissociation and ignoring the Milner effect. Bjerrum also used experimental data on the catalysis of esterification by hydrochloric acid. The experimental facts were that the rate of esterification is within the experimental accuracy directly proportional to the stoichiometric concentration of hydrochloric acid. It was generally accepted that the catalysis is due to hydrogen ion and there was no reason to suppose that the rate was not directly proportional to the concentration of hydrogen ion. It follows that the hydrochloric acid is completely ionised.

As already mentioned, Arrhenius was violently opposed to this modification of his ionic theory. Whether owing to the opposition of Arrhenius or owing to a general epidemic of shortsightedness among the physical chemists of that generation, Bjerrum's theory was not generally accepted until most people had forgotten its origin.

The years intervening between the two papers on complete dissociation were both active and fruitful. In the summer of 1910 Bjerrum spent a month in Perrin's laboratory. He made quantitative measurements on the Brownian movement of rubber-latex particles in a glycerol-water mixture having a viscosity a hundred-fold that of water. The results led to the value of Avogadro's constant previously obtained by Perrin and so showed that the law of equipartition of energy of the particles is unaffected by the viscosity of the medium. This visit to France was a great joy to Bjerrum's

wife who had been to school in France and always remained a Francophile.

In the spring of 1910 Nernst visited Copenhagen and invited Bjerrum to spend a year in his laboratory in Berlin. Thanks to a grant from the Carlsberg Foundation he was able not only to accept but also to take his wife and baby son with him. This year 1911 was one of the highlights of Bjerrum's life. He had no teaching duties and was free to devote himself entirely to research and study. He worked on the determination of the heat capacity of various gases at high temperatures by the explosion method. He improved the apparatus and introduced corrections for errors hitherto unnoticed. What is more important he became interested in explaining the temperature-dependence of gaseous heat capacities. He did this successfully by applying the quantum theory of a harmonic oscillator to the internal vibrations of molecules. The expressions which he first formulated for the total energy of linear and nonlinear molecules are still used today. This is the earliest known example of correlation between a measured macroscopic quantity, the heat capacity, and a completely molecular quantity, the characteristic frequency. Thus did Bjerrum become the pioneer of the new kind of science on the borderland between physics and chemistry. In 1933 it was given the name "Chemical Physics."²

Through gaseous heat capacities Bjerrum became interested in the internal degrees of freedom of molecules and so in their infrared spectra. He made a fundamental contribution to general theory in the particular case of HCl. It had been shown that HCl had an absorption band at 2800 cm^{-1} due to vibrational motion and also a broad band in the far-infrared region at 67 cm^{-1} ascribed to rotational motion. Bjerrum predicted that through combination of vibrational and rotational motions the absorption band in the near-infrared region should have two peaks at approximately $(2800 - 67)$ and $(2800 + 67)\text{ cm}^{-1}$ respectively. Almost a year later this prediction was confirmed experimentally by Burmeister. This phenomenon is still called a Bjerrum double band. More refined measurements made shortly afterwards by von Bahr showed that each of the two bands, now called *P*-band and *R*-band respectively, can be resolved into a series of equally spaced lines.

In 1912 Bjerrum was promoted to become docent (tutor) while

retaining at the same time the post of assistant (demonstrator) to Professor Biilmann.

In the summer of 1914 Bjerrum succeeded Odin T. Christensen, lately deceased, as professor of chemistry in the Royal Veterinary and Agricultural College where he remained until his retirement in 1949 and where he continued to work until a few days before his death. Many people have expressed the opinion that it was wasteful for such a brilliant scientist to devote so much of his life to teaching veterinary and agricultural students, but Bjerrum himself considered good teaching as important as good research. No one could be more painstaking than Bjerrum in teaching, especially elementary teaching. Some of his scripts are models of perfection. Particularly worthy of mention is his book "Inorganic Chemistry" which includes a comprehensive but elementary exposition of all the fundamentals of physical chemistry. The book went through six editions, the first in 1916 and the last in 1956. Nearly ten thousand copies have been sold in all. The third edition, in which Brønsted's definitions of acids and bases were adopted for the first time in a text-book, was translated into German in 1933, into Russian in 1935, and into English by R. P. Bell in 1936. Equally impressive for clarity and comprehensiveness, but on a higher plane, is a paper published in 1917, entitled "On acid and basic reaction." This paper includes a rigorous, yet simple, analysis of the factors determining the accuracy of an acid-base titration, i.e., concentration, pK_a of the two reactants, pK_a of the indicator. For anyone with a taste for clear thought and accurate exposition this paper is a delight.

It must not be concluded from the above remarks that when Bjerrum became a professor his teaching responsibilities, which he took so seriously, interfered with research in his department. Quite the contrary, but naturally and gradually less experimental work was done with his own hands and more with those of his juniors.

Bjerrum attracted research workers from several lands and more than a dozen became professors: England (Guggenheim), Finland (Sihvonen), Germany (Ebert, Manegold, Heitler), Hungary (Zechmeister), Norway (Schreiner), Poland (Józefowicz), Sweden (Brosset, Bäckström, Larsson, Ljunggren, Widmark). This distribution is undoubtedly due largely to the fact that most of

Bjerrum's published papers are written either in Danish or in German. By contrast Brønsted published mostly in English and almost all the visitors to his laboratory were American or English.

Nearly all Bjerrum's work after he became professor is related to electrolytes. I have already mentioned the work with Faurholt on the hydrolysis of chromic compounds. With the collaboration of Lannung he made an extensive experimental and theoretical study of the distribution between two solvents of, on the one hand, alkali halides and, on the other, the inert gases. The ratio of the distribution coefficients of these two classes of substance is related theoretically to the permittivity of the medium and the size of the ions. The extent of agreement between theory and experiment is unimpressive, probably because the macroscopic permittivity accounts inadequately for the interaction between ion and solvent. What is of special interest from a general thermodynamic point of view is that the well-known expression of Born was shown by Bjerrum to relate to the free energy and not to the total energy as previously supposed. This is not the only occasion when Bjerrum corrected a mistake, in what is now called statistical thermodynamics, by a world-famous physicist. In the original papers of Debye and Hückel on interionic attraction they gave the right formula for the free energy but their formula for the total energy was wrong and was corrected by Bjerrum.³ These two mistakes are both examples of an incomplete understanding of the fundamental role of free energy as the most secure connecting link between statistical mechanics and thermodynamics. The clarification of this by Bjerrum in these two particular cases was finally and completely generalized by Onsager.⁴

Another much earlier contribution to the thermodynamics of solutions was the derivation from the Gibbs-Duhem relation of the formula relating the activity coefficient γ (first mentioned in print by Noyes and Bray in 1911 but attributed by them to G. N. Lewis) to the osmotic coefficient ϕ (first introduced by Bjerrum in 1916). The use of this formula leads to values of γ from freezing-point measurements which give directly values of ϕ .

In 1919 Bjerrum and his assistant Gjaldbaek published a paper on the acidic and basic properties of soil, which raised the study of soils from pure empiricism to a science. At that time it was

fashionable to measure the pH of anything one could lay one's hand on, but there had been little, if any, attempt to interpret the experimental pH values. Bjerrum and Gjaldbaek pointed out that to understand the acidic and basic properties of a soil it was not sufficient to measure its pH; equally important was the manner in which the pH is changed on the addition of strong acid or alkali. In other words, complete titration curves were required. Moreover, the details of such titration curves would depend on the conditions of the titration, such as the rate of titration, the temperature, the presence or absence of carbon dioxide, the acid or base used (since insoluble precipitates might be formed). When all such experimental information had been obtained, it should be possible to correlate it with the acid-base equilibria of the substances in solution and with the solubility equilibria of the solid phases present. Bjerrum and Gjaldbaek accordingly formulated a programme involving a systematic study of the part played in soil equilibria by the important slightly soluble solids. The programme was a tremendous one and will probably never be completed, but its conception and commencement was the first milestone in a new science. In connexion with this programme Bjerrum himself became especially interested in the several forms of calcium orthophosphate, and his last work was a monograph on this subject published in his eightieth year.

In 1923 Bjerrum made a discovery of outstanding importance for the physical chemistry of proteins. It was well known that an α -amino-acid exists in strongly acid solution as the cation $^+\text{H}_3\text{N}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ and in strongly alkaline solution as the anion $\text{H}_2\text{N}\cdot\text{CHR}\cdot\text{CO}_2^-$. It had always been assumed that the intermediate form preponderant near the isoelectric point was the neutral molecule $\text{H}_2\text{N}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$. Bjerrum, by elementary reasoning based on the numerical values of the two acidity constants, showed that the intermediate form is in fact the "ampho-ion" $^+\text{H}_3\text{N}\cdot\text{CHR}\cdot\text{CO}_2^-$. This deduction, once made, was so obviously right that one could not but wonder that it had not been self-evident. Yet no less an authority than Michaelis had written in 1922 concerning the amino-acid ampho-ion "*Seine Menge ist zweifellos auch stets verschwindend klein.*"

In 1926 Bjerrum contributed an important modification to the

theory of ionic interaction given by Debye and Hückel in 1923. In its original form the theory contains the assumption that configurations in which the mutual potential energy of a pair of ions exceeds kT are negligibly rare. This assumption is valid for 1:1 electrolytes but not for 2:2 electrolytes in water, while in solvents with much smaller dielectric constant it is not even valid for 1:1 electrolytes. Bjerrum showed how this restriction can be avoided by treating separately and differently the interaction between (a) pairs of ions distant apart more than $z^2e^2/2\epsilon kT$ and (b) pairs of ions distant apart less than $z^2e^2/2\epsilon kT$ (in which class only pairs of oppositely charged ions need be considered). The interaction (a) can be completely taken care of by the formulae of Debye and Hückel modified only to exclude the ion pairs accounted for under (b). The interaction (b) was taken care of in a simple approximate manner as a short-range interaction analogous to a chemical equilibrium. This method of extending the theory to higher valencies and lower dielectric constants is simpler than any of the alternative methods and at least as effective. Bjerrum conventionally called the ions of (a) "free ions" and those of (b) "associated ion pairs." This terminology has unfortunately been misunderstood and misinterpreted.

In 1929 Bjerrum and his assistant Augusta Unmack published a two-hundred-page paper describing several years' work on the measurement and interpretation of electromotive force of cells containing a hydrogen electrode in various dilute aqueous solutions, a standard calomel electrode, and a bridge of concentrated potassium chloride: in other words, the type of cell associated with the name of Sørensen and the expression pH. The solutions contained hydrochloric acid or sodium hydroxide or a phosphate buffer or a citrate buffer or a glycine buffer. A wide range of concentrations was covered with various concentrations of added sodium or potassium chloride. Measurements were made at four temperatures. From these measurements, by judicious estimation of the effect of the liquid-liquid junctions and careful extrapolation to infinite dilution, values were obtained for the thermodynamic ionization constant of water and for the thermodynamic equilibrium constants of eight other acid-base equilibria. Each of these constants was determined over the range of temperature from 0° to 37° C., and

the heat changes of the several acid–base equilibria were deduced. These values are of necessity not quite as accurate as those obtainable by cells without liquid–liquid junctions, but for several of the acid–base equilibria and at several of the temperatures the values obtained by Bjerrum and Unmack are after thirty years still the best available.

I have mentioned briefly less than a score of the odd hundred publications of Bjerrum. I hope this suffices to establish my contention that Bjerrum was without any comparison the most versatile physical chemist of his generation. In 1949 a collection of his most important papers, translated into English, was published to celebrate his seventieth birthday.

In 1931 Bjerrum was offered the chair of inorganic chemistry at the University of Copenhagen, but being well settled and happy at the Agricultural College he preferred to stay there. Over the period 1939 to 1946 Bjerrum was director of the Royal Veterinary and Agricultural College. This was a period of unprecedented strain owing to the five-years' occupation by the Germans. Bjerrum retired from his chair in 1949 and had the satisfaction of being succeeded by his able assistant Aksel Tovborg Jensen. After retirement Bjerrum continued his research work and indeed was able to resume work which he had been compelled to set aside when he had been too busy with administrative duties. In 1951 he published a fifty-page article entitled "Structure and properties of ice." The positions of the oxygen atoms in ice are unambiguously determined by X-ray diffraction but the positions of the hydrogen atoms were still a matter of controversy. This late paper by Bjerrum shows that he still retained his full power for original thought. His last paper, published in 1958, was a monograph on the solid calcium orthophosphates, a continuation of work which he had to put aside twenty years earlier.

The death of his charming and versatile wife in 1934 was a terrible shock for Professor Bjerrum from which he seemed never to have completely recovered. Fortunately there remained four children of whom he was justly proud. The eldest is his brilliant son Jannik born in 1909 (the same year as the theory of complete dissociation of electrolytes). Niels Bjerrum's three attractive daughters are all happily married. Niels Bjerrum's greatest joy in his

last years was being a fifteen-fold grandfather. Jannik's eldest boy and another grandson are appropriately named Niels.

Bjerrum was elected to membership of the Royal Danish Academy in 1916 and was its treasurer from 1927 to 1931. He became honorary member or corresponding member of over twenty learned societies including the Chemical Society (1938) and honorary doctor of Göttingen and Åbo.

Niels Bjerrum had three great loves: the first, his wife and family; the second, physical chemistry; the last, but perhaps not the least, sailing. Strictly speaking, the last had precedence for it began when he was only ten years old, spending his summer holidays at his maternal grandfather's home in Kolding. Throughout his life Bjerrum spent his summer holidays sailing. In 1927 he became a member of the Royal Danish Yacht Club. During the terrible years of the German occupation, when the open sea was barred, it was a great solace still to be able to sail in the Ise Fiord. Not until he was over seventy did Bjerrum consent, with some reluctance, to have a boat with a motor.

In the morning of Thursday, September 25th, 1958, Bjerrum was working, as was still his custom, in the library of the chemistry department where he had spent over forty years of his life. That afternoon he had a stroke and he died on Tuesday, September 30th. Thus ended abruptly and peacefully in its eightieth year the life of a great man. No one who knew Bjerrum can lament the suddenness of his death. His life was happy and active to the end.

Of Bjerrum's personal characteristics the following were outstanding. He was profoundly interested in everything around him, and his scientific curiosity was insatiable. He was intolerant of tyranny, arbitrariness, hypocrisy, pomp, conceit, and loose thinking, but tolerant of almost everything else. If he seemed to some people impatient, the explanation is that he expected others to be as reasonable as himself and in this he was unduly optimistic. He had all the qualities of a leader and he knew it. Above all he was kind. He will be sadly missed by his many friends.

I am grateful to Professor Tovborg Jensen and to Fröken Unmack for furnishing certain details concerning Bjerrum's life and work. Above all I am grateful to Professor Jannik Bjerrum for let-

ting me have a copy of his father's autobiographical notes, which were invaluable in the preparation of this Lecture.

NOTES AND REFERENCES

- 1 Lewis, *Z. phys. Chem.*, 70, 215, 218 (1910).
- 2 See *J. Chem. Phys.*, 1, 1933, editorial.
- 3 Since the obituary lecture was delivered, Dr. Redlich has reminded the author that this mistake was corrected independently by Gross and Halpern (May 1925), by Adams (October 1925), and by Bjerrum (November 1925).
- 4 Onsager, *Chem. Rev.*, 13, 73 (1933).

From The Niels Bjerrum Memorial Lecture delivered before the Chemical Society on October 15, 1959, printed in the Proceedings of the Chemical Society, March, 1960, page 104, and shortened by the author.

E. A. GUGGENHEIM

.. 108 ..

Irving Langmuir

1881-1957



SCIENTIFIC WORK

IRVING LANGMUIR'S scientific work covered a period of fifty years, starting in 1904 with his doctorate dissertation at Göttingen "Ueber partielle Wiedervereinigung dissociierter Gase im Verlauf einer Abkühlung" and terminating in 1955 with an unpublished report on "Widespread Control of Weather by Silver Iodide Seeding." Between these two extremes his work exhibits a great diversity of interest and achievement, and can be grouped into seven categories. This grouping follows rather closely that used by Langmuir himself in the Introduction to "Phenomena, Atoms and Molecules," a reprint¹ of some twenty of his papers selected by him in 1950. The dates associated with each category indicate when most of the relevant work was published, although it will be clear from the span of some of these dates that Langmuir's productive interest in certain areas continued throughout a large part of his active scientific life. The categories are as follows and are listed, as nearly as possible, in rough chronological order.

Publication dates

1906 to 1921	Chemical Reactions at High Temperatures and Low Pressures
1911 to 1936	Thermal Effects in Gases
1919 to 1921	Atomic Structure
1913 to 1937	Thermionic Emission and Surfaces in Vacuum
1916 to 1943	"Chemical Forces" in Solids, Liquids, and Surface Films
1923 to 1932	Electrical Discharges in Gases
1938 to 1955	Science Out-of-Doors

1. *Chemical Reactions at High Temperatures and Low Pressures.* In 1904 Langmuir commenced his doctoral work at Göttingen and Prof. W. Nernst suggested as a thesis subject the study of the formation of nitric oxide from air in the vicinity of a glowing Nernst filament. It was thought that the filament would act catalytically

on the reaction between oxygen and nitrogen and that the final equilibrium would correspond to the temperature of the filament. This method of studying equilibria looked extremely attractive because of the simplicity of the apparatus involved as compared with the complexity of the equipment more generally used in such studies. This simple hypothesis proved not to be applicable to the interaction of nitrogen and oxygen in the vicinity of a glowing Nernst filament and the thesis effort was shifted to studying other gaseous equilibria, such as the dissociation of carbon dioxide brought about by a glowing platinum filament, where the hypothesis was found to be valid. This very early work is especially interesting as a foreshadowing of Langmuir's predilection for experiments requiring only simple apparatus but where understanding of the experimental results might involve new, bold concepts and extended theoretical analysis. In this case the work led to an understanding of the unexpectedly much greater importance of thermal conduction, as compared with convection, in determining the heat loss from a filament through the first few tenths of a millimeter of gas surrounding it.

This thesis work was also important in orienting Langmuir's scientific interests in July, 1909, when, at Dr. W. R. Whitney's invitation, he came to the relatively new Research Laboratory of the General Electric Company. Dr. Whitney suggested that Langmuir should spend a few days looking around the laboratory to see what was going on; the first entry in his notebook reads:

July 19–July 21, Spent these two days looking thru lab and seeing what work was being done.

Apparently these two days (or was it three?) were sufficient to show Langmuir that the laboratory was intensely interested in problems connected with making good incandescent lamps out of the the new ductile tungsten wire just introduced by W. D. Coolidge. The first experiments of his choice were therefore concerned with preparing pure hydrogen and studying the effects of heating tungsten wire in it. At that time all incandescent lamps were vacuum lamps and the general feeling was that if the vacuum could be made better the life of the lamp would be improved. Langmuir, on

the other hand, had been impressed with how much better lamp-factory vacuum was than university vacuum and, not knowing how to improve this, resolved to see what effects the opposite approach of adding various gases would have on the life of tungsten lamps. He was also impressed with the ready availability of tungsten wires capable of being heated electrically to very high temperatures, and from this environment of good vacuum and high-temperature filaments grew his important scientific work on chemical reactions at high temperatures and low pressures. These studies included the discovery and detailed investigation of the formation of atomic hydrogen by contact of molecular hydrogen with a hot tungsten filament, a careful analysis of the effects of water vapor in incandescent lamps, and a systematic investigation of the mechanisms of "clean-up" of oxygen, nitrogen, and other gases at low pressure by hot tungsten and molybdenum filaments.

2. *Thermal Effects in Gases.* This work was a logical outcome of the studies of chemical reactions in lamps described in the preceding section. Langmuir had established that, apart from the special chain reaction with water vapor, the life of a tungsten vacuum lamp was insensitive to the residual gases usually present and was determined entirely by the evaporation of tungsten. This encouraged him to experiment with lamps containing much higher pressures of inert gases and to study heat losses from filaments under these conditions. He found that the evaporation of tungsten in nitrogen at approximately atmospheric density is essentially a diffusion process and obeys laws similar to those of conduction or convection of heat from a wire; that is, for wires of small diameters, the actual amount of tungsten evaporated is almost independent of the size of the wire, an unfavorable result for the very small filaments used in most lamps. On the other hand, experiment showed that, for several reasons, life and efficiency were better for large filaments in nitrogen. This dilemma was resolved by coiling the small wire tightly into a helix of substantially larger diameter, a form of construction which led to widespread adoption of the gas-filled lamp.

The dissociation of hydrogen by a hot tungsten filament had been postulated by Langmuir to explain the sudden increase in heat loss

from a filament in hydrogen at high temperatures. Estimates of the heat of dissociation were made and some properties of atomic hydrogen were observed, such as its adsorption on a cold glass wall. Several years later Langmuir's attention was attracted by R. W. Wood's preparation of concentrated atomic hydrogen in an electric discharge tube and Wood's observations on the heating effects produced by the recombination of the atomic hydrogen on a variety of surfaces. This led Langmuir to the invention of the atomic hydrogen welding torch, in which large amounts of atomic hydrogen are produced by an arc between tungsten electrodes in hydrogen and the atoms are allowed to recombine on the metal to be heated.

3. *Atomic Structure.* Some of Langmuir's most productive thinking was guided by consideration of the differences between what he called "physical forces" and "chemical forces." This thinking led to his concept of the adsorption process and also to his rather brief sortie into the field of atomic structure during 1919 to 1921. The Bohr theory was then well established by reason of its spectacular spectroscopic successes. Langmuir considered this to be a typical "physical force" theory based on forces acting according to simple laws between mathematical points separated by relatively large distances. The chemist, on the other hand, did not think of molecules as point centers of force but rather as complex entities having structures which made the outward acting "chemical force" at one part of the molecule quite different from that at another. Moreover, the "chemical forces" were usually of shorter range than the "physical forces." This thinking, together with G. N. Lewis' theory of the "cubical atom" and a keen feeling for the complex chemical phenomena to be explained, led Langmuir to his "octet theory" of atomic structure in which Bohr's centrally orbiting electrons were replaced by electrons distributed in regions throughout the atom, each electron being stationary in its region or describing a restricted orbit within the region.

With these concepts, and a limited number of postulates, Langmuir was able to correlate a tremendous variety of chemical phenomena. Further detailed calculations, however, led to the need for more assumptions and it was not long until the advent of

quantum-mechanical concepts of chemical bonds led him to transfer his efforts to other problems. Langmuir, while appreciating the great conceptual contributions made by quantum mechanics, was impressed by the tremendous mathematical difficulties of attempting to understand chemical properties in detail by this route. Because of this he apparently made a decision not to develop a working knowledge of these new tools for himself but to continue his work where more classical methods were still fruitful.

4. *Thermionic Emission and Surfaces in Vacuum.* As a natural outgrowth of his earlier work on tungsten lamps, Langmuir entered the field of thermionic emission in 1913 to answer the specific problem of why relatively large electron currents did not appear as shunt currents from the negative leg to the positive leg of a tungsten lamp with a hairpin filament. At that time the true origin of thermionic emission was still in doubt, and there were even suggestions that the thermionic electrons were by-products of a chemical reaction and, therefore, that the absence of the shunt current in lamps was due to the very high vacuum. Langmuir made experiments with lamps containing two separate hairpin filaments and soon arrived at the concept that the shunt currents were small because the charges on the electrons in the space between the legs of the filament shielded the negative leg from the accelerating field due to the positive leg. This hypothesis was at once submitted to theory and calculation resulting in the Child-Langmuir² space charge equation, according to which the electron current between electrodes of any shape in vacuum is proportional to the $3/2$ power of the potential difference between the electrodes. This celebrated law was followed through in great detail for various electrode configurations, and corrections for the initial thermal velocities of the electrons were introduced. The $3/2$ power law became the major issue in a hard-fought patent suit.

Thorium oxide is added to tungsten lamp filaments to improve their mechanical behavior at high temperatures, and it had been observed sporadically that abnormally high thermionic emission was obtained from some lamp filaments. Langmuir undertook a systematic study of this problem; he soon showed that the ab-

normally high emission was definitely associated with the presence of thoria in the filament, and worked out in great detail the temperature treatment needed to obtain thoriated emission and the magnitude of the emission under various conditions. His theoretical study of the phenomenon showed that the enhanced emission could be explained in terms of the formation by diffusion of a single, more or less complete layer of thorium atoms on the surface of the filament. These rather detailed and involved concepts were obtained by interpretation of experiments with the simplest of vacuum tubes and current measurements with a portable microammeter.

It is interesting to observe here that the interpretation of such simple experiments, even in the hands of so great a master, can at times be incorrect in detail. Langmuir interpreted the transient behavior of the surface film in formation as being due to a combination of the diffusion of the thorium atoms through the tungsten lattice plus a reasonable assumption of "induced evaporation" when a new thorium atom arrived under one already in the surface layer. It was not until considerably later that more complicated experiments by P. Clausing showed that the thorium really diffused to the surface through the intercrystalline material and then spread over the surface from these lines of access in a two-dimensional diffusion.

Another extended series of thermionic studies, done in collaboration with K. H. Kingdon and J. B. Taylor, involved new phenomena observed when cesium is put into a vacuum tube containing a tungsten filament. At low filament temperatures, and particularly if the filament is first coated with a monatomic layer of oxygen, the cesium atoms are strongly adsorbed from the vapor onto the surface of the filament. Such a Cs-O-W surface is the most efficient thermionic emitter known, and high hopes were entertained at first for its application in radio tubes. However, the advent of conventional barium oxide cathodes heated from the alternating current supply replaced this possible application.

Another new phenomenon observed was that, at higher filament temperatures, cesium atoms (ionizing potential 3.9 volts) striking a tungsten filament are robbed of an electron by the filament (work function 4.5 volts) and come off as positive ions which may

be collected at a negative electrode. Langmuir gave a theoretical interpretation of these phenomena in terms of his concepts of adsorbed films and the Saha equation. This equation gives the equilibrium concentrations of ions, electrons, and neutral atoms at a known temperature in a gas with known ionization potential, and for this application must be modified to include the electron emitting capability of the hot filament, since this shifts the temperature equilibrium. Langmuir had great hopes for the use of this controlled source of ionization for neutralizing electron space charge in power tubes, but experiment, and later theory, showed that only modest effects could be obtained. The principle of ionization at a hot surface found early application as a molecular beam detector and at present is being investigated as a source of ion propulsion for space vehicles.

All kinds of studies and processes requiring evacuated enclosures were aided tremendously by Langmuir's invention of the condensation pump. This pump was simple to construct, had very high speed and, with the aid of refrigerants, produced an extremely high vacuum. It rapidly came into widespread use.

5. *"Chemical Forces" in Solids, Liquids, and Surface Films.* This area of science is one to which about one-quarter of Langmuir's publications are devoted and for which he received the Nobel prize in 1932. His ideas on the short-range character of "chemical forces" led him to a new concept of adsorption in which every molecule striking a surface remained in intimate contact with the surface for a short or long time and then evaporated. This adsorption contact was so intimate that it might be thought of as a chemical bond, and thus the concept of a firmly held, single layer of adsorbed atoms replaced the existing idea of a relatively thick adsorbed sheath extending some distance out from the surface with concentration decreasing with distance.

Langmuir made an early application of his ideas on surface films to the study of films on water surfaces, an area of science to which his attention had been drawn by the beautifully simple experimental techniques developed over the years by Miss Pockels, Lord Rayleigh, Devaux, and Marcelin. Langmuir made a tremendous extension of this technique by the introduction of a surface

balance method for measuring the spreading force of the films; he showed that these films were truly monomolecular. In collaboration with Katharine Blodgett and V. J. Schaefer, a whole series of techniques was developed for working with surface films and used to study gaseous, liquid, and solid films, including such complicated molecules as proteins.

Langmuir's ideas on adsorbed films were also applied to films on solids and led to the development of the Langmuir adsorption isotherm, which gives an expression for the fraction of the surface covered by the adsorbed layer in terms of ambient pressure and a temperature dependent variable characterizing rates of condensation and evaporation at the surface. A theory was developed for the catalytic effect of an adsorbing surface which considered the chemical reaction as actually occurring in the adsorbed film and elucidated many features of such reactions which had hitherto been obscure. This theory became the basic approach to surface kinetics.

6. *Electric Discharge in Gases.* In 1914 mercury arc rectifiers were in common use, and Langmuir gradually became interested in some of the scientific problems of electric discharges in gases. Langmuir was impressed with the opportunities for electron tubes capable of controlling high power and endeavored to apply the newly understood phenomena of vacuum electron amplifier tubes to the much larger currents of gas tubes. E. F. W. Alexanderson pointed out in conversation that in alternating current power circuits the important thing was to be able to control the initiation of the current in any part of the circuit and that if this were done the circuit reversal of voltage could be used to extinguish the current at a later time in the cycle. This led Langmuir, in 1914, to the idea of inserting a grid in a mercury arc device to control the starting of current to a main anode. The study of such devices was carried on in collaboration with A. W. Hull and others.

Langmuir's activity in the gas-discharge field developed rather slowly, but in 1923 he was analyzing the current-voltage characteristics of currents to probe electrodes placed in a mercury arc. He found that the current to a negatively charged plane collector was independent of voltage over a wide range and showed by

gridding tests that the current was due to the arrival of positive ions rather than the emission of photoelectrons. The independence of voltage was explained in terms of a plane parallel "positive ion space-charge sheath" in front of the plane electrode, whose thickness increased with voltage in accordance with the $3/2$ power space-charge law, but whose outer surface was entered by an invariant stream of positive ions.

This initial work with collecting electrodes, or probes, led to a most fruitful series of experiments in collaboration with H. M. Mottsmith, Jr., and Lewi Tonks. The current-voltage characteristics of probe electrodes of all sorts were studied experimentally and theoretically, the results being used to elucidate the mechanism and behavior of electric discharges in gases under a wide range of conditions. One of the most important concepts arising from this work was the interpretation of the volt-ampere characteristic of a probe collecting electrons in terms of a Maxwellian temperature distribution of the electrons. The temperatures found were very high, of the order $15,000^{\circ}\text{K.}$, and showed that the electrons were continually receiving energy from the drift gradient in the discharge and were far from being in temperature equilibrium with either the positive ions or the neutral gas. The production of ionization in the discharge could be explained quantitatively in terms of the ionization effectiveness of the electrons in the high energy Maxwell tail.

Langmuir and Tonks also made a study of electrical oscillations in an ionized gas. Langmuir was so impressed with the implication of organization and structure in the ionized gas evidenced by the capability of oscillation that he adopted the word "plasma" to indicate the fundamental nature of a volume of ionized gas essentially free of space-charge. At the same time he was much impressed with the instabilities and the energy transfer capabilities of a plasma, properties which have come to the fore in recent studies of fusion plasmas.

7. *Science Out-of-Doors.* Langmuir had a keen and continuing interest in the scientific basis of outdoor phenomena. One of the earlier examples of this was his explanation of the streaks or wind-

rows of seaweed and bubbles which form on the ocean parallel to the direction of a moderate wind. He had noticed this phenomenon especially during an Atlantic crossing in August, 1927, and studied windrows for several years at Lake George, New York, where he had a summer camp. By simple but carefully planned experiments, using such apparatus as oriented umbrellas and lamp-bulb floats, Langmuir was able to establish that the windrows were caused by wind-induced circulation of the surface water, the water on the surface flowing toward the windrows, downward under them, and up again at a point halfway between them.

An extended series of experiments with V. J. Schaefer was devoted to the production of particles of various desired sizes in atmospheric air, their behavior in filters, and the development of apparatus for generation of oil smokes for military use. The resulting smoke generator was of the order 100 times more effective than existing generators and was adopted by the United States forces in World War II.

Another series of studies with Schaefer concerned the nucleation of ice crystals in supercooled clouds by seeding with particles of solid carbon dioxide; Schaefer showed that the low temperature is the important thing. This led to a great deal of outdoor experimentation related to possible modification of the weather by such processes and was the last field of science in which Langmuir took an active part.

PERSONAL AND WORK CHARACTERISTICS

The diversity of Langmuir's scientific work shows his great breadth of interest and also indicates his characteristic approach, which was to seize on some unusual phenomenon or technique, exploit this until the returns showed signs of diminishing, and then pass on to something else. Examples of this were his realization that the ready availability of tungsten filaments and good vacuum conditions offered an excellent opportunity for the study of chemical reactions at high temperatures and low pressures; his attack on the random, anomalously high electron emission observed from tungsten filaments containing thorium; his appreciation of the

possibilities of the surface tension trough for the study of surface film phenomena coupled with the insight which his ideas on localized "chemical forces" gave him into the fundamentals of the problem; and his realization of the power of the probe characteristic technique for studying the mechanism of electric discharge in gases.

This brilliant insight into fruitful directions for applying his effort was coupled with the characteristic of being a tremendous worker. Although not by any means a slave to science, science was never far from his thoughts, whether in the laboratory, at home, traveling or out-of-doors.

Perhaps the best demonstration of this work effort is given by Langmuir's notebooks. During his 37 active years in the laboratory, Langmuir filled 54 notebooks of 330 pages each with the details of his scientific work. These notebooks exhibit the vast foundation of data, theory, and numerical calculation on which the structure of Langmuir's published scientific work was erected. There was always a notebook with him and he wrote in it at any time, even in a sleeping-car berth. His records were especially detailed regarding the genesis of ideas and must have been the delight (or the embarrassment?) of all patent lawyers who encountered them.

Langmuir combined his unusual scientific ability with a strong practical bent and was always on the lookout for practical applications of any idea or new piece of knowledge with which he came in contact. For example, he was keenly aware of the great opportunities for electron tubes capable of controlling power circuits and his notebooks contain detailed schemes for using "trapped ions" and cesium thermions for neutralizing electron space charge. Both of these possibilities were later made obsolete by the development of controlled plasma tubes. Langmuir made 138 personal patent disclosures, of which 63 led to issued patents. Some of these were of great practical importance, such as the gas-filled lamp, high-vacuum electron tube principles, the condensation pump, the thoriated tungsten filament, atomic hydrogen welding, the grid-controlled arc, and the military smoke generator. Much of Langmuir's scientific work lay in areas where there was little scope for patent protection, but whenever the opportunity existed Langmuir was quick to recognize it.

Langmuir had well-developed abilities as an applied mathematician. His notebooks are filled with theoretical work related to his experimental investigations and with the results of extended computations made in test of the theories. Most of these computations were on the desk-computer scale since much of his work was done before the advent of large computers.

Most of Langmuir's scientific work was accomplished with the assistance of relatively few people. He never directed a large research team. In much of his earlier experimental work he was assisted by Samuel P. Sweetser, whose name appears in many of the early publications. Sweetser prepared the experimental equipment and, with meticulous care, took volumes of characteristic curves for analysis by Langmuir. At one time when the electron emission studies were very active, Langmuir's notebook gave a list of some 82 experiments which he was interested in having Sweetser do. With such a backlog of work it would seem that the direct experimental staff might have been expanded, but apparently Langmuir preferred not to do this.

This may have been partly because Langmuir was usually closely connected with experimental work by some of the younger scientists in the laboratory, as noted elsewhere. These younger people were often working on problems suggested by Langmuir but had opportunity to contribute to the work according to their own talents instead of working under very close supervision.

In addition to these activities, the notebooks are filled with suggestions for work made to many people inside and outside the laboratory who were not at all directly connected with Langmuir. In this way, without formal organization, his scientific influence touched a great many people.

Langmuir's personal characteristics may be described by such words as sincerity, intensity, vigor, intellectual integrity, breadth of interest, depth of approach. His speech was rapid, emphatic, and filled with the intensity of his interest in the ideas which he was trying to convey. In spite of these hard-driving characteristics Langmuir was always approachable and willing to give his best attention to any sensible problem brought to him. If he passed you in the hall without recognition this was not a demonstration of aloofness, but

rather of his complete absorption in the current scientific problem. If the problems of others demanded too much of his time he could always retire to his study at home until his own current idea was satisfactorily advanced. Monday morning was frequently dedicated to an exposition of the scientific developments of the weekend to those who he thought might be interested.

The photograph of Langmuir communicates the atmosphere of the laboratory and reveals a little of his breadth of scientific interest. The large bottle at the upper left corner contains a colloidal suspension of vanadium pentoxide used in some polarization studies, the shelves are filled with surface active chemicals, and the inner surface of the glass bulb is flecked with crystals from a nucleation-adsorption study.

Langmuir was an enthusiastic skier and mountain climber and for several years owned and piloted an airplane.

BIOGRAPHICAL

Irving Langmuir was born in Brooklyn, N. Y., on January 31, 1881, the son of Charles and Sadie Comings Langmuir. His mother was a descendant of the Lunt family, which came to this country on the "Mayflower." After obtaining elementary education in public schools in Brooklyn, he traveled with his parents to Paris, where he studied for three years. He then returned to the United States, studied for a year at Chestnut Hill Academy, Philadelphia, then in Brooklyn at Pratt Institute, and at the School of Mines, Columbia University. In 1903 he graduated from Columbia with a degree in metallurgical engineering. Again he visited Europe, this time to study at the University of Göttingen in Germany, where he was awarded M.A. and Ph.D. degrees in 1906.

Until July, 1909, he taught chemistry at Stevens Institute of Technology. He then joined the staff of the General Electric Company's Research Laboratory at Schenectady, N. Y., to begin his colorful career in scientific research.

Dr. Langmuir and his wife, the former Marian Mersereau of South Orange, N. J., whom he married in 1912, made their home at 1176 Stratford Road, Schenectady, N. Y., with a son, Kenneth, and a daughter, Barbara.

HONORS

Among scientific honors that were bestowed upon him, the Nichols Medal, awarded by the New York Section of the American Chemical Society, was twice given to Langmuir, once in 1915 for his work on chemical reactions at low pressures, and again in 1920 for his work on atomic structure.

The Hughes Medal of the Royal Society of London was awarded him in 1918 for his researches in molecular physics. In 1920, the American Academy of Arts and Sciences gave him the Rumford Medal for his thermionic researches and for his development of the gas-filled incandescent lamp. In 1925, the Royal Academy of Lincei at Rome, Italy, bestowed upon him the Cannizzaro Prize. In 1928 he was the recipient of the Perkin Medal, and in 1930 he was awarded the Chandler Medal and the Willard Gibbs Medal.

In 1932, Langmuir became the first American industrial chemist to be awarded the Nobel Prize, granted him for researches in surface chemistry. In the same year, Popular Science Monthly Magazine awarded him its annual medal and honorarium of \$10,000 as "an American who has done notable scientific work."

The Franklin Medal of the Franklin Institute and the Holly Medal of the American Society of Mechanical Engineers were given him in 1934, and the City of Philadelphia presented him the John Scott Award in 1937. In 1940 he received a plaque as a "Modern Pioneer of Industry" from the National Association of Manufacturers, and in 1943 became an honorary member of the British Institute of Metals. In 1944, Langmuir became the fourth American to receive the coveted Faraday Medal of the British Institute of Electrical Engineers.

The Mascart Medal of the Société Française des Electriciens was presented to Langmuir in 1950. He was a foreign member of the Royal Society of London and a fellow of the American Physical Society. He had served as president of the American Chemical Society, and as president of the American Association for the Advancement of Science.

He was also an honorary member of several societies, including the Chemical Society of London. Langmuir held honorary degrees from the following colleges and universities: Northwestern, Union,

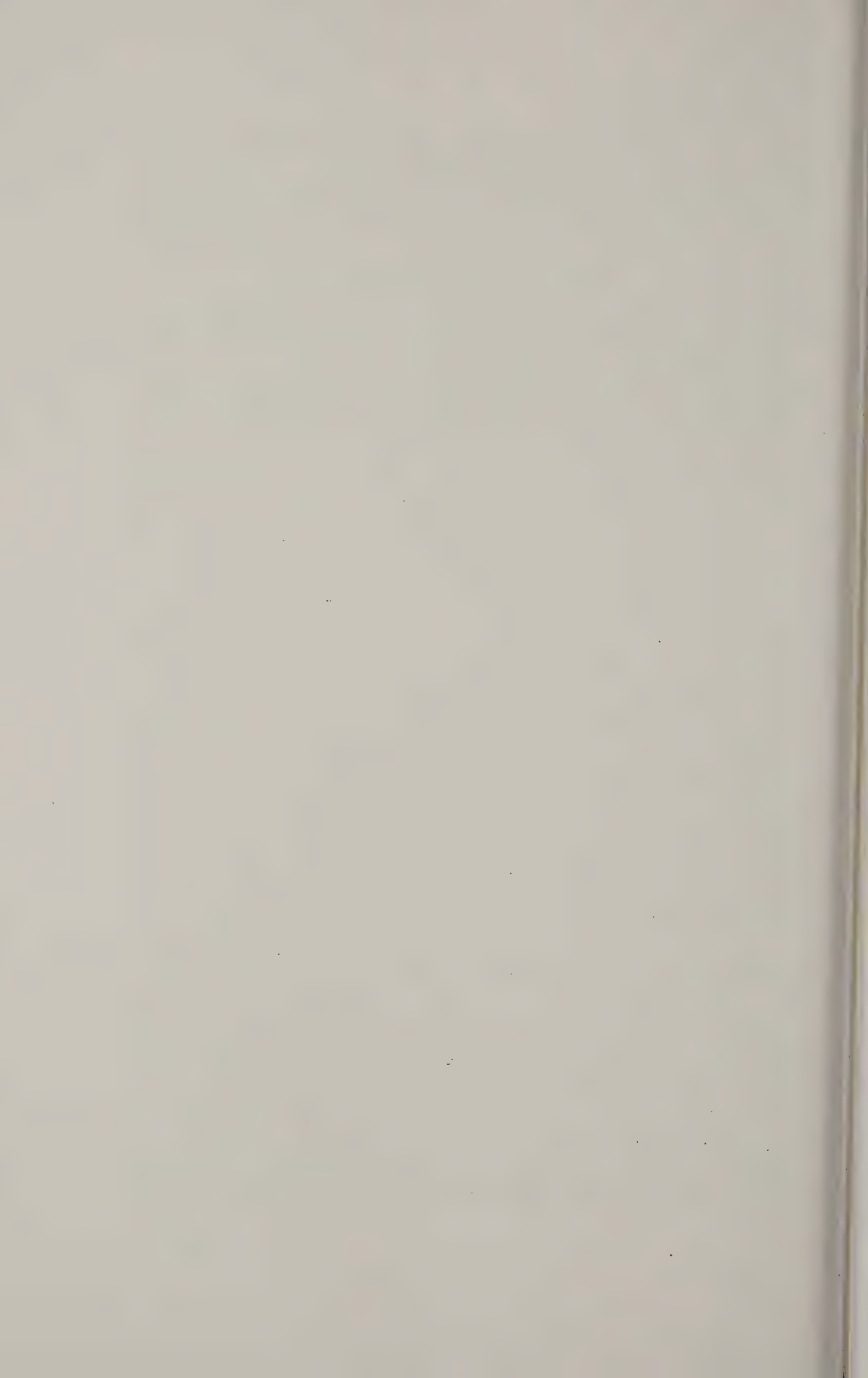
IRVING LANGMUIR

Edinburgh (Scotland), Columbia, Kenyon, Princeton, Lehigh, Harvard, Oxford, Johns Hopkins, Rutgers, Queens (Canada), and Stevens Institute of Technology.

NOTES AND REFERENCES

- 1 Philosophical Library, New York (1950). A complete reprinting of Langmuir's papers, together with critical comments and biographical material, will be published soon by Pergamon Press.
- 2 Independent derivations of this equation were made by Langmuir for electrons, and by C. D. Child for positive ions about two years earlier.

K. H. KINGDON



.. 109 ..

Hans Fischer

1881-1945



C
t
V
S
Y
S

HANS FISCHER was born at Höchst am Main on July 27, 1881. His father had a responsible position at the dye factory there and later also in Biebrich. Hans obtained his doctor's degree in 1904 at Marburg under Theodor Zincke (1843–1928). After completing a course in medicine, he became assistant to Emil Fischer in Berlin. Then Friedrich von Müller (1858–1939), who had tried to find a relationship between the pigments of bile and those of blood, and had come to Munich in 1902, invited Fischer to join him there. Hans Fischer accepted the position at the medical clinic to work in this new field of research which required close cooperation between medicine and chemistry.

It is to the great credit of Friedrich Müller that he did not burden his chemical protégé with clinical duties but, instead, allowed him to devote himself entirely to scientific pursuits. The same credit should be given to the physiologist Otto Frank (1865–1944), in whose laboratory Fischer took an assistantship before the beginning of the First World War, a position which involved no teaching studies.

At this time, Oscar Piloty, Adolf Baeyer's son-in-law, was also studying the chemistry of the bile pigment bilirubin. This engendered a certain amount of tension and prevented the two young rivals from entering into closer personal relations with each other and the associates at the University of Munich.

The external conditions were favorable in every sense for Fischer's scientific activity, and almost his only worry lay in procuring adequate amounts of steer gallstones as the raw material from which to prepare bilirubin. From the start, Fischer worked entirely independently. The writer has never heard that Fischer ever sought any advice in chemical matters. He was not inclined to discuss his plans nor the results of his researches before they were published. During the many years of our friendship, he seldom spoke of the way his work was going. It was the custom in those years for chemists to keep their current researches in complete secrecy in order to protect the field from intrusion by others; many

teachers solemnly swore their doctorate candidates to exercise discretion. In my opinion, the exchange of ideas that is the general practice in research laboratories now is much preferable to the former custom, even though there is a certain danger of loss of priority.

Shortly after the outbreak of World War I, Adolf Windaus was called from Innsbruck to succeed Otto Wallach at Göttingen. Fischer took over the vacant chair of medical chemistry at Innsbruck in 1915. Fritz Pregl, Adolf Windaus, and Hans Fischer have brought fame to this modest, small laboratory. No further advance was made there with respect to bilirubin after the valuable progress achieved in several directions at Munich. The war made experimental activity difficult. The marvelous scenery around Innsbruck enticed the young chemist to go on long walks and, in the winter, to slip away into the wonderland of snow. The sudden and tragic death of his father clouded the lighter moments of the years at Innsbruck. While making a not very dangerous climb of a peak in the Zillertal Alps, the elder Fischer fell into a covered crevasse, from which he could not be saved despite the efforts of the Alpine herdsman who was summoned at once. The unfortunate victim had been brought almost to the edge of the crevasse when his strength gave out! Before the eyes of his son, he fell back into the chasm and was irretrievably lost.

The following years, Hans Fischer spent as head of the Institut für Medizinische Chemie of the University of Vienna, as successor to Ernst Ludwig (1842–1915). Because of the war and its consequences, this was not a propitious time for pure research. However, in the spring of 1921, he took over the direction of the Institut für Anorganische Chemie at the Technische Hochschule (Technical University) at Munich, and there he quickly cleared away the external and internal hurdles. In an incredibly short time, he organized the laboratory from which issued his impressive work for twenty-four years. There was some doubt at that time of the wisdom of calling a medically minded chemist to a technical university. The doubts proved to be unjustified. The development of the Fischer school at Munich demonstrated the importance of the scientific personality at the head of a laboratory. The medical man from Vienna not only accomplished much pure research at the

Munich Technical University, but he trained there many excellent chemists for industry and science. Those who came from the Hans Fischer laboratory and had been so thoroughly trained to carry out experimental studies were well received everywhere, especially at the great dye manufacturing plants; many of these young men eventually rose to be leaders in chemical industry. Numerous others from Fischer's school distinguished themselves in academic careers.

In marshaling all of the resources of his laboratory into research activities, Fischer introduced much that was new and exemplary. The usually rather difficult preparation of the innumerable compounds that were needed in large amounts as intermediates in the tortuous paths of the syntheses provided the students with valuable exercises. Great stress was laid on purity and yields. A staff of microanalysts had to take care of tremendous numbers of samples. No other institute had ever turned out so many new compounds. Special laboratories were set up for measuring absorption spectra, for calorimetric determinations, and later for taking x-ray diagrams. The conscientious study of the current literature constantly inspired Hans Fischer to try out and introduce new methods.

The problem of the structure of hemin, i.e., of the colored components of the blood pigment, was attacked in Munich even before the nature of the bile pigments, especially bilirubin, had been cleared up. The previous studies by Marcel Nencki, Wilhelm Küster, Richard Willstätter, Oskar Piloty, and others had shown that the two groups of substances are chemically closely related. The structure first proposed by Küster for hemin was rejected vigorously by Hans Fischer at the start, but the subsequent synthesis of this pigment forced him to acknowledge his error. After the analytical method, namely, the study of the pyrrole derivatives obtained by the reductive cleaving of hemin, had produced no well-defined structure for the starting compound, Fischer began to put the pyrrole segments together in mosaiclike arrangements and then to weld together, by brilliant synthetic procedures, the semi-molecules of the pyrromethenes produced in this manner. The hemin problem was solved in 1929 by several methods of synthesis; the 1930 Nobel Prize for chemistry was awarded to Hans Fischer for this work.

However, the problem of the structure of the bile pigments and

their synthesis was not solved until much later. The discovery that bilirubin is formed in the organism through oxidative fission of the porphin ring with loss of a methine group led to the answer which had been sought by Friedrich Müller in the 1890's.

From the start, Hans Fischer had set for himself the goal of combining the analytical elucidation of the natural pyrrole pigments with the systematic exploration of all the phases of the chemistry of the parent substance, namely, pyrrole. What he accomplished as a result of this endeavor would, in itself, have been enough to constitute the lifework of an extensive chemical career.

The ring skeleton of porphin, which is made up of four pyrrole nuclei bound to each other by methine groups, has been entrusted by nature to perform some of her most essential biological tasks. The blood pigment carries oxygen, in loose combinations, to all of the living cells and assures their metabolism. The respiratory enzymes, which likewise are porphin derivatives containing coordinatively bound iron, bring about the chemical action of the oxygen, an action that, in essence, consists in the reoxidation of the bivalent iron formed from the trivalent iron during the dehydrogenation processes.

No less important is the third porphin derivative, chlorophyll. Its role need not be discussed here, but the mere fact that in chlorophyll magnesium takes the place of the iron in the respiratory enzymes reveals the difference in the functions of the two groups of natural products.

Willstätter, who was then a Privatdozent at the University of Munich, began to study chlorophyll in 1902. He was the first to isolate and purify the two components of chlorophyll, namely, the bluish-green chlorophyll-a and the yellowish-green chlorophyll-b, to make them accessible by preparative methods. He also showed that chlorophyll contains two carboxyls esterified with methanol and phytol; by reductive cleavage of the pigment, he arrived at substituted pyrroles similar to those already known from hemin. The transformation into porphyrins was also accomplished. Although no insight into the inner structure of chlorophyll was obtainable at this stage, Willstätter left the field. Today, it is difficult to understand why almost twenty years went by before anyone took up where Willstätter left off in 1912. After he had established

the structure of hemin, Hans Fischer was almost impelled to turn to the chlorophyll problem. This was done with the full consent of Willstätter, who had returned to Munich in 1916 as head of the Chemical Institute of the University of Munich.

The structural differences between chlorophyll and hemin appear slight. One of the four pyrrole rings is partially hydrogenated, and between it and its neighbors, there has attached itself, from a side chain, a fifth ring, namely, an isocyclic outer ring. This was sensed rather soon in superb intuitional manner by Hans Fischer, whereas the hurdle of the divergent degree of saturation in one of the pyrrole rings impeded the progress of the study for some time. Today, we have clearly before us the results of the gigantic task of unraveling the structure of chlorophyll. A few partial steps in the complete synthesis are still lacking. These will doubtless be supplied soon because three of his best students have banded together to finish the task as a memorial to their revered teacher.

On chlorophyll alone, Hans Fischer published 129 papers. They are not easy reading, even to those familiar with the topic. He was not particularly concerned with literary style, and furthermore the relationships are often not brought out clearly. Usually, important findings are not properly stressed. Even in his later years, Hans Fischer had to cope with embarrassment when lecturing. It often happened that an important success, which should have been highlighted, was relegated to the status of an incidental remark in a subordinate sentence. In his retiring and withdrawn manner, he lacked all sense for the importance of external expressions and impressions, and this shows up clearly in the lack of form and emphasis in his oral and written reports.

Those who met Hans Fischer for the first time probably concluded from his massive, compact build and from his energetic, duel-scarred face that he was a decidedly dynamic person. In a physical sense this was quite correct. He was skilled in all kinds of sports; he was an excellent mountain climber and skier. This physical dexterity and endurance was all the more remarkable because he was tubercular from his twentieth year on, necessitating the removal of a kidney in 1917. He had to fight the onslaught of this disease on his spine for the rest of his life. His exceptional vitality always prevailed. He required no recreation, and the idea

of rest was foreign to him. His short vacations were usually spent on long and strenuous automobile trips. His mode of life was extremely moderate and unassuming in all respects. In his early years, it was his custom to carry his luggage with him in a knapsack, even when on lecture trips abroad; this included even the inevitable frock coat. The adjustment of his behavior to the accepted social customs was improved somewhat under the influence of his wife, who was about thirty years his junior, and with whom he enjoyed a very happy married life. Contrary to his usual reticence, he once told me how much his life had been enriched by his marriage despite the great difference in their ages.

The unwavering devotion to his research activities, a real *furor experimentalis*, dominated him to such an extent that hardly any other interest could gain a footing—except his love of nature and his passion for wheeled vehicles which he had maintained from the bicycle through all the various stages of the development of the motorcycle and automobile. He had no connections with art; music played no part in his life.

In scientific questions, Fischer was very sensitive. He watched over his wide field of work with a careful eye and was always ready to meet opponents with his sword bared. Differences that involved his findings could stir up his usually even temperament and turn his pen into a feared weapon. And yet this man of iron will and inflexible bodily strength was innately a tender, sensitive person, who attracted all who came to know him intimately. Although he despised all sentimentality, he felt a strong need to help where he could and to the extent of his abilities, no matter who appealed to him. The responsibility for and to his students lay closest to his heart; their unlimited devotion to him provided the most convincing testimony of the warm-hearted human understanding that shone from his light blue eyes.

This brief characterization of Hans Fischer has admittedly not exhausted the full depth of his real nature. The direct reasons that led to the sudden, voluntary termination of this meaningful life lay entirely beyond anything that might have been anticipated even by those who knew him best. The calamitous events of the closing years of World War II were obviously too much for his powers of resistance, whose weakening had already become apparent to some

HANS FISCHER

degree. The ringing of the Easter bells could no longer restrain him from taking the final step. Thus, there passed from this world a man, who, like few others, was capable of being the support and leader of German science. The date was March 31, 1945.

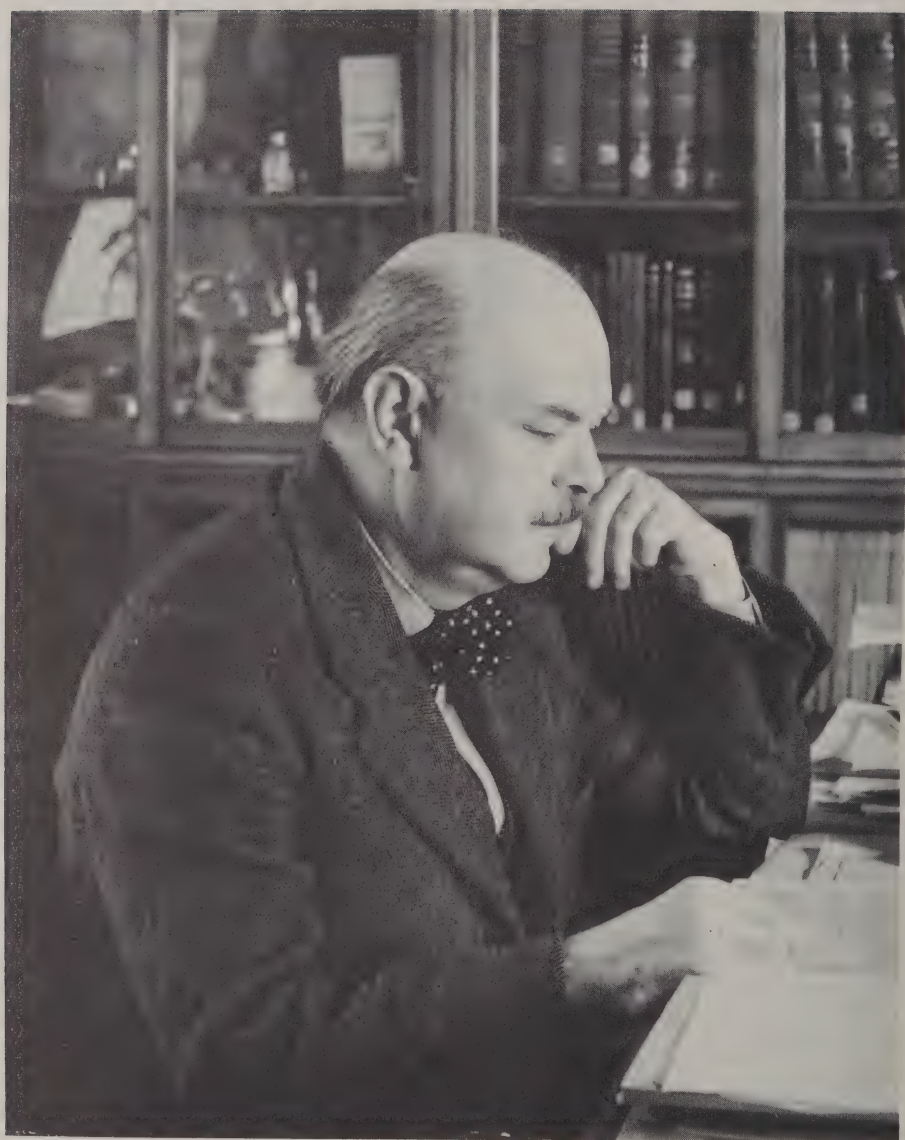
From: *Angew. Chem.*, 62, 1 (1950). Translated by Ralph E. Oesper.

HEINRICH WIELAND

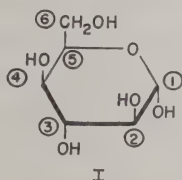
.. 110 ..

Claude Silbert Hudson

1881-1952



THE name of Claude S. Hudson is listed among the great leaders in the development of the chemistry of the carbohydrates. His main contribution was the establishment of the stereochemical nature of the labile hydroxylated carbonyl or cyclic hemiacetal function of the sugars and the concomitant development of the relations between structure and optical rotatory power in this group of stereoisomers. Thus, in the case of glucose (I), Emil Fischer¹ established the basic stereochemistry of carbons 2 to 5, the ring size was established by Haworth,² Hirst,³ and associates, and the stereochemical assignment to carbon 1 was made by Hudson.



Although essentially all of his work was carried out in various laboratories of the United States government, he nevertheless established his mark as a great teacher. His published work attracted many young men to study in his laboratory and to come under his inspirational tutelage. His personality was very forceful and most unusual. It was cloaked in an outer sheath of informality and gracious manner, but his associates knew that under this was a strong critical spirit holding them and himself to exacting standards of scientific performance. His work was his life and his life was his work. After periods of intense concentration he was able to relax with kindred spirits and rejuvenate himself for the next round of intense scientific activity. He had a complete disregard for conventions and was, in all respects, a true creative artist. He was a great writer in his specialty and was an even greater speaker. He could apply a relatively simple organic reaction to the carbohydrates and hold an audience completely spellbound by describing to them the results he had obtained. He never spoke from notes but

always offered a thoroughly logical and polished presentation. As an informal raconteur he was without peer, and this gift had its root in his background in the leisurely life of the old American deep South with its emphasis upon good manners and pleasant conversation.

Hudson came of early American southern stock that was a mixture of English, Scotch, Irish, and Huguenot French. His maternal great-grandfather and grandfather were physicians and the latter, John S. Wilson (1821–1892), was a surgeon in the 40th Georgia Regiment of the Confederate Army. His paternal great-grandfather, Robert Hudson (1786–1861), was a wealthy plantation owner in Williamsburg County, South Carolina. Hudson's paternal grandfather and father lived in South Carolina but in the disturbed period following the close of the war between the States, his father entered the mercantile business and at one time was the president of the Mobile Fertilizer Co., of Mobile, Alabama. It was in this beautiful southern city on the shores of Mobile Bay that Claude Hudson spent his childhood and early youth, a period upon which he looked back with fond nostalgia. Claude had been born in Atlanta, Georgia, but was moved as an infant to Greenville, Alabama, and shortly thereafter to Mobile. The French influence in this Gulf Coast region was prominent, and Hudson recalled the Mardi Gras festivities which were similar to those of New Orleans. His father's home in Mobile comprised four acres with six beautiful live oaks shading its long entrance way. There was a large vegetable garden in the rear and Claude was early introduced to the cultivation of plants. His mother was interested in church and charitable work and the son planned to enter the Presbyterian ministry. He received a good secondary school education in private schools in Mobile where he came under the influence of two excellent teachers, Mr. Julius T. Wright and the Rev. Archibald C. Harte.

At sixteen, Claude Hudson arrived at Princeton University to initiate his college work in preparation for the ministry. Thereafter he was to spend all of his time in the North and was to return to his beloved Alabama only on occasional visits. While he always enjoyed these returns, he was in later life irked and disappointed at the cultural and economic backwardness of this area

of the states. The reasons for this state of affairs were complex but were in no small measure due to the tendency of their inhabitants to look backward upon vanished glories rather than forward to new challenges. Claude's arrival at Princeton also initiated a love and devotion for this institution which remained with him to the end of his life; indeed his mortal remains are interred in his beloved Princeton village. Never had any college a more devoted and loyal alumnus!

At Princeton, Hudson elected a course in chemistry given by Professor L. W. McCay, who offered brilliant showmanship in lecture demonstrations. Thereupon the Presbyterian ministry lost a candidate and the science of chemistry gained a votary. His college chum, a minister's son, said: "Console yourself by believing that you have conferred a favor on your imaginary future parishioners!" Hudson received the B.Sc. degree *cum laude* from Princeton in 1901 and was rewarded with an endowed fellowship (Class of 1860) in experimental science. He embarked immediately upon scientific research. While recrystallizing some milk sugar for Professor William F. Magie,⁴ of the department of physics, to be used by him in measuring the specific heat of its aqueous solution, Hudson encountered the phenomenon of mutarotation⁵ and immediately proposed its study for his investigational problem. This was not agreeable to the professor of organic chemistry who stated that Emil Fischer had just completed his studies with the sugars and there were no problems left in that area. It was then agreed that the student could use the laboratory facilities of the chemistry department but could report his results to Professor Magie and take his M.Sc. degree in the department of physics; this was done in 1902. Then followed a year of study in Germany, in accordance with the custom of the times.

Hudson began his studies abroad with Professor Walther Nernst⁶ at Göttingen but spent the following summer semester with J. H. van't Hoff⁷ in Berlin. In Germany, Hudson continued his work on the mutarotation of lactose, later published, and did not accept an assigned problem from either professor. In addition, he proposed to Professor G. Tammann of Göttingen the measurements which resulted in the publication of the now famous closed-ring curve

solubility relation in the nicotine-water system. Hudson attended an International Chemical Congress at Berlin in the summer of 1903 and there met Emil Fischer, whose work in organic chemistry did not at the time especially interest Hudson. He did meet Arthur A. Noyes, from the United States, who offered him a position in the newly established Research Laboratory of Physical Chemistry at the Massachusetts Institute of Technology. This Hudson was pleased to accept since a stringency in his father's finances eliminated further study abroad. This year of study in two of the great European universities of the time was a fruitful period. The contact with van't Hoff, although short, was especially stimulating. A fine relationship existed between these great research professors and their students. Hudson and another American taught Nernst the intricacies of the game of poker prior to the professor's visit to the United States on a mission concerned with patent rights on the Nernst lamp. On being told of the dangers of Indian scalplings in the vicinity of New York, the eminent professor observed that his baldness absolved him from any such fears.

On Hudson's return he worked for one year (1903-1904) as a research assistant in Boston with A. A. Noyes and W. R. Whitney. Again he continued on his own path with further studies on the mutarotation of sugars and elaborated his theory of the maximum rate of solution whereby the rotation of an unknown anomer⁸ could be evaluated by measuring the solubility and polarimetric changes with time in a solution saturated with respect to the known anomer. The grant for this fellowship originated with the Carnegie Foundation and when the renewal application listed studies in the preparation of rare sugars to be used in the measurements, the whole approach was considered to be too "organic" in nature and the grant was not renewed, even though the proposal carried the signed recommendations of Nernst and van't Hoff.

After this experience with the Leipzig-trained American physical chemists, Hudson turned to physics and Professor Magie, who obliged him with an instructorship in physics at Princeton (1904-1905) and then helped him to obtain a similar post at the University of Illinois which he held from 1905 to 1907. This was no better and Hudson approached the newly appointed head of the

Illinois Chemistry Department, W. A. Noyes, who promptly informed him that he did not qualify as a chemist. Meanwhile Hudson had married (1906) Miss Alice Abbott of Urbana and they were having difficulties, even at that time, in living on his salary of \$900 per year. A Göttingen chum then helped him obtain a position in the technologic branch of the U. S. Geological Survey at a salary of \$1600. On his way to accept this post, he stopped at Princeton to take the final examination for the degree of Doctor of Philosophy. At the time, this title was taken rather literally and a member of the department of philosophy was required to sit in on the examination in physics, a discipline which was considered to be a branch of the subject of natural philosophy. Professor A. T. Ormond represented the philosophy department; his specialty was the history of philosophy, on which subject he had written a book. A hasty perusal of this by Hudson failed to assure him of success and he bethought himself of the mile walk the professor was required to take from his home to the university. Hudson stated, "I can see now his beaming, round countenance when I appeared at his home with horse, victoria and colored coachman to drive him in regal splendor to the examination hall." The scientific part of Hudson's examination passed off brilliantly and Professor Ormond declined to question. The candidate was dismissed and some considerable time later Professor Magie emerged to inform him that he had been awarded the degree *magna cum laude*. Hudson then politely asked if he might inquire why the committee took so long in arriving at the decision. The reply was, "Oh, it was because of that philosophy professor, he was holding out for a *summa cum laude*."

While Hudson was at Princeton to complete his Ph. D. work, he spent a few days in the laboratory of Dr. G. A. Hulett, who had just been appointed professor of physical chemistry. In this time he measured the pH dependency of the mutarotation of D-glucose and established the formulation

$$k = 0.0096 + 0.258[\text{H}^+] + 9750[\text{OH}^-].$$

This equation shows that the catalytic activity of hydroxyl ions is 40,000 times that of hydrogen ions and the first term allowed the ionic dissociation of water to be evaluated as 1.0×10^{-14} at 25°.

In 1907 Claude Hudson made the acquaintance of Dr. Harvey W. Wiley, then chief of the Bureau of Chemistry of the United States Department of Agriculture, and in 1908 Hudson was appointed chemist aid to Mr. Frederick Weber in the laboratory concerned with the analyses involved in Dr. Wiley's famed "poison squad" tests of food preservatives. Wiley had once carried out research in the technology of cane sugar and during a slack period in the analytical work, Hudson persuaded Wiley to allow him to conduct some investigations on the action of invertase on sucrose. Hudson then completed the work, one of the first of its kind, which showed that this enzymic reaction followed the laws of mass action. Thereafter, Wiley allowed Hudson to conduct research of his own choice and provided him with an assistant, H. S. Paine, the two of them forming a new section designated the physical chemistry laboratory. There resulted his famous series of articles on the action of invertase on sucrose in which it was shown that the reaction was not reversible and that the D-fructose component was combined in sucrose in an unusual form. He also published (1909) his famous paper entitled "The Significance of Certain Numerical Relations in the Sugar Group" wherein he enunciated his rule, originally empirical, that the more dextro-rotatory member (D-series) of an anomeric pair was to be designated α and its hydroxyl, or substituted hydroxyl, was to be written to the right in the Fischer projection formula:



This paper further contains his rules of isorotation which state that if the rotation is divided into that A contributed by the anomeric center and that B of the remaining centers, then in any anomeric pair the sum of their molecular rotations is a constant characteristic of the B portion and the difference is a constant characteristic of the A part.

$$\begin{aligned} \text{For the } \alpha\text{-D anomer, } A + B &= [M] \\ \text{For the } \beta\text{-D anomer, } -A + B &= [M] \end{aligned}$$

In 1910 he published his lactone rule wherein he demonstrated that the asymmetric center concerned in the ring closure controlled the rotation. It was later shown that in acyclic aldonic acid functions the center adjacent to the carboxyl function controlled the rotation. These rules have some limitations but have been extremely useful to the chemist. They established an early reputation for Hudson and in 1916 he was recognized by the award of the Nichols Medal of the New York Section of the American Chemical Society. On a later visit to the department of chemistry of the University of Illinois, Professor Roger Adams invited Dr. Hudson to sit in on the oral examination of a candidate for the degree of Doctor of Philosophy. On being asked by Professor Adams to state Hudson's rules the candidate replied that he only knew one, to wit, "Any drink with gin in it is a good drink." Dr. Hudson then remarked that the answer was correct since this was also one of his rules (gin being free of aldehydes and fusel oil) and he had indeed expounded it to the candidate on the previous evening.

In 1911, Dr. Wiley resigned from the Bureau of Chemistry and was replaced by Dr. C. L. Alsberg, who backed Dr. Hudson even more and placed him in charge of a carbohydrate laboratory with an augmented staff.

From 1911 to 1912, Hudson was away from Washington on leave of absence substituting for Professor G. A. Hulett at Princeton, who was in turn on leave of absence in Washington. At Princeton, Dr. Hudson attracted a graduate student, Julian K. Dale, and they initiated their classical measurements on the kinetics of mutarotation of the α and β forms of D-glucose. Hudson taught a course in physical chemistry at Princeton which consisted of a résumé of his own researches followed by instruction in the reading of German chemistry. On his return to the Bureau of Chemistry, Hudson embarked upon an intensive period of research (1912-1919) with a number of co-workers. He initiated his valued series of publications on exact methods of preparation of sugars from natural sources. He found a new source for melezitose and discovered (with F. B. LaForge) the new heptulose "sedoheptose" in *Sedum spectabile*. They became interested in this common garden plant because a large bed of it was growing in Hudson's

home flower garden and they could find no record of an examination of the sap of the plant for sugars. Many years later this sugar was established (M. Calvin) as an important member of the photosynthetic carbon cycle in all green plants. Hudson turned to the acetate esters of the sugars for a rich source of readily preparable and crystallizable anomers and in the course of this investigation found that the sugar galactose could exist in more than one ring form by the preparation (made with J. M. Johnson) of its four isomeric pentaacetates in two anomeric pairs.

During World War I Hudson initiated experiments in the preparation of activated carbon for gas masks at Trenton, New Jersey, in association with Professor W. F. Magie of Princeton and Dr. Edward Mack, Jr., who had just completed his Ph.D. work with Professor G. A. Hulett. This interest in activated carbon persisted and led to the only deviation from carbohydrate research undertaken by Dr. Hudson. He left the government service to act as a consulting chemist-in Trenton where he was concerned with the manufacture of activated carbon and with malt sirups of the prohibition era. Dr. J. K. Dale was associated with him in this work which extended over the period 1919–1923, with one year added later in 1924 for consulting service in the Hawaiian Islands related to the use of activated carbon in the pineapple canning industry. Brewing was a subject of personal interest to Hudson; during the prohibition era he made his own home brew according to an exacting procedure with excellent results. After his retirement from the government service many years later, he continued this interest by acting as a consultant to the Anheuser-Busch Brewing Co. of St. Louis.

In 1923 Mr. Frederick J. Bates, chief of the Polarimetry Section of the National Bureau of Standards in Washington, D. C., offered Hudson a research position for the study of sugars which Hudson gladly accepted; he remained there until 1928. This period was notable for the attraction to his laboratory of fellowship students from this country and abroad: A. Kunz, E. Pacsu, C. B. Purves, W. C. Austin, and the writer. Dr. Hudson worked with his own hands and seemed mainly concerned with a large assortment of small beakers in each of which he was attempting to crystallize a

sirup. These beakers did not appear to be labeled but he knew what was contained in each. He was an early riser and walked to the laboratory with a sandwich in his pocket which, with a quart of delivered milk, served for his lunch; it was partaken while watching experiments so that no time was lost over the lunch period. He never returned in the evening but utilized this time for writing and study. He interested one of the physicists, an expert in optics, in his sugar experiments and published a number of papers with him. While Hudson was away on a trip, I discussed the purification of a sugar derivative with this eminent physicist and mentioned that the main impurity present was acetamide. He inquired about the optical rotatory power of acetamide. On being informed that it had none he was very skeptical and I was forced to bring out the books and back my statement. This was not easily done, as nowhere in the description of acetamide was there any mention that it was optically inactive. Indeed, I am not sure whether I convinced him at all.

When I was at the Bureau of Standards, one of the storeroom attendants had published a paper with Hudson. It was said that at one time Hudson interested a janitor in his experiments so much that the man took out a subscription to the *Journal of the American Chemical Society* in order to follow the publications of the laboratory as they appeared.

The writer studied with Hudson just as long as Hudson had studied with van't Hoff—that was for one summer. The impact of his personality and creative artistry, however, was tremendous and was unequaled by any other experience I have ever had. During this period, Hudson initiated his program on the higher-carbon sugars in a search for members having the upper structures of the very rare aldoses. He discovered (with A. Kunz) the configurational inversion, by aluminum chloride, of the second and third carbons in the reducing portion of the disaccharides lactose and cellobiose. Studies on the kinetics of the hypobromite oxidation of aldoses were initiated with H. S. Isbell.

In 1929 Hudson accepted an invitation to continue his work on a larger scale in the Hygienic Laboratory (later the National Institutes of Health) of the United States Public Health Service.

The position carried the title of Professor of Chemistry, and so at long last Hudson had achieved a professorship. He enjoyed telling the academic professors that he was no ordinary professor but was a professor by Act of Congress. At the 1926 Meeting of the American Chemical Society, the rather pompous and always highly critical Professor Harold Hibbert of McGill made the public statement that it was unfortunate Hudson did not hold an academic post, whereupon Hudson arose and remarked that there were *some* universities in which he would not care to hold a professorship. During the move to the laboratory at Bethesda, Maryland, Hudson quietly took along several kilograms of melezitose which he had prepared from "gritty honey." This caused a great uproar, at the Bureau chief level, which eventually subsided.

At this time Hudson had published a new classification of sugar ring types based upon deviations from his isorotation rules. Thus, methyl α -D-mannoside was assigned a furanoside structure because its A_{OMe} value was in disagreement with that of the methyl D-glucosides for which Hudson accepted a pyranoside structure. This came into conflict with the methylation studies of Haworth and Hirst in England, and both sides presented their cases before the Conference on Carbohydrates of the International Union of Chemistry at Liège, Belgium, in September, 1930. The English investigators presented a valid proof independent of rotatory considerations, and Hudson returned to the United States to spend much time in a fruitless attempt to prove that methyl α -D-mannoside was a mixture or molecular compound. Together with E. L. Jackson, he then applied the periodate α -glycol-splitting agent of Malaprade to verify the methylation experiments in a most elegant manner and, in addition, to correlate the configurations of the anomeric carbons of the methyl pyranosides of the pentoses and hexoses. The results gave an experimental verification of the 1909 assignments which had been based on optical rotatory power alone. In spite of this scientific disagreement, the personal relations between Hudson, Haworth, and Hirst remained eminently cordial.

The period at Bethesda, from 1929 to his retirement at the age of seventy in 1951, was extremely productive with emphasis on organic structural and synthetic aspects of the sugars. He had

many co-workers from both the government service and from visiting fellows. Through Dr. C. H. Herty of the Chemical Foundation, a well endowed fellowship was placed in Hudson's laboratory and filled by a succession of worthy young men. Hudson's principal assistant during this period was Raymond (Ray) M. Hann. He was an indefatigable worker who understood Hudson and his methods and kept the whole group in smooth operation. For example, Hudson was notorious for not answering such letters as were considered by him to involve routine or trivial matters, but any letter addressed to Ray Hann would be tactfully brought to the attention of Hudson and answered promptly by Ray. The researches of the laboratory in this period covered many topics and are recorded in over 200 journal publications.

Although Hudson often remarked that he was accepted as a colleague by neither the physicists, the physical chemists, nor the organic chemists, he was a regular attendant at the meetings of the American Chemical Society and particularly enjoyed those held in the southern cities. A favorite whimsey of his was that on occasion an L-Hudson could be brought out from behind the mirror. D-Hudson was the serious, sober, gentlemanly scientist. The L-Hudson was the convivial one who partook of intoxicating beverages, was strongly attracted by beautiful women, and was in general sinful. On the occasion of the Organic Symposium of the American Chemical Society at Richmond, Virginia, L-Hudson was in charge. It became necessary for him to leave the auditorium, but alas, the only inconspicuous exit was a spiral staircase which was dextro-rotatory. With the aid of friends he finally mounted it, but claimed ever after that he had been racemized in the process.

Hudson was elected chairman (1934) of the Organic Division of the American Chemical Society, but in later years he was closely associated with the Carbohydrate Division. With William B. Newkirk and Norman F. Kennedy he organized (1939) the Starch Round Table, an annual meeting held in some secluded spot under the auspices of the Corn Industries Research Foundation. Hudson showed little interest in organic chemistry not directly connected with the carbohydrates. On the other hand, he was intensely critical of physical chemists who attempted to

grapple with the problems of polysaccharide chemistry without exhibiting any knowledge or appreciation of the established organic structures of these substances.

Hudson was associated with the *Advances in Carbohydrate Chemistry* from its inception in 1944; this is an annual journal publishing review chapters. He insisted that a high level of scholarship be maintained in this endeavor. He served as an associate editor of the *Journal of the American Chemical Society* and was a close friend of its great editor, Arthur B. Lamb.⁹ He spent much time reviewing manuscripts in the carbohydrate field and insisted on holding their authors to the same rigid criteria by which he judged his own writings, an excellent principle but one not always appreciated by the contributors. When the editorship of the journal changed, one of Hudson's manuscripts in his internationally famed series of sugar preparations was returned to him with the statement that the improvements cited, which indeed made the difference between crystals or no crystals at the finish, were of insufficient novelty to warrant space in the journal. The resultant near-volcanic eruption in the suburbs of Washington was such that this decision was hastily reconsidered and the paper entitled "Improvements in the Preparation of L-Arabinose from Mesquite Gum" appeared under his name alone in 1951 as the last in this great series of authoritative publications.

Claude Hudson was married four times, the first three marriages ending in divorce. His last marriage, in 1942, was to his childhood sweetheart, the then-widowed Erin Gilmer Jones of Selma, Alabama.

In addition to being the recipient of the Nichols Medal (1916) mentioned previously, Claude Hudson was the recipient of the Willard Gibbs (Chicago Section, American Chemical Society, 1929), Richards (Northeastern Section, 1940), Borden (American Chemical Society, 1941) and Cresson (Franklin Institute of the State of Pennsylvania, 1942) Medals, the Hillebrand Prize (Washington Chemical Society, 1931) and the Sugar Division Citation (1946). He was elected to membership in the National Academy of Sciences (U.S.A.) in 1927, and to the Kaiserlich Leopoldinisch-Carolinisch Deutsche Akademie der Naturforscher

(Halle) in 1932. He was a charter member (1936) of the Academy of Medicine of Washington, D.C., and was an honorary fellow of the Chemical Society (London). He received the honorary degree of D.Sc. from Princeton University (1947), the grand prize of \$10,000 from the Sugar Research Foundation of New York (1950), and the first Federal Security Agency Award (1950).

Hudson survived official retirement by only two years and died in his Washington apartment of a coronary thrombosis on December 27, 1952. His scientific work will long stand as a monument of rigorous mathematical reasoning, exceptional clarity, and experimental cleverness. His influence upon carbohydrate chemistry and upon the rising science of biochemistry was great and profound.

GENERAL REFERENCES

- C. S. Hudson, Autobiography in "The Collected Papers of C. S. Hudson," R. M. Hann and N. K. Richtmyer, eds., Vol. I, Academic Press, New York, 1946, pp. xi-xxviii.
- R. M. Hann and N. K. Richtmyer, eds., "The Collected Papers of C. S. Hudson," Academic Press, New York, Vol. I, 1946, 898 + xxxv pp., Vol. II, 1948, 795 + xvi pp.
- E. L. Hirst, The Hudson Memorial Lecture, *J. Chem. Soc.*, 1954, 4042-4058.
- M. L. Wolfrom, "Claude Silbert Hudson," *Advances in Carbohydrate Chem.*, 9, xiii-xviii (1945).
- L. F. Small and M. L. Wolfrom, "Claude Silbert Hudson," Biographical Memoirs, National Academy of Sciences of the United States of America, XXXII (1959), pp. 181-220.

NOTES AND REFERENCES

- 1 "Das Buch der Grossen Chemiker," Band II, G. Bugge, ed., Verlag Chemie, Berlin, 1930, p. 408 ff.
- 2 Walter Norman (Sir Norman) Haworth (1883-1950), Nobel laureate in chemistry, 1937, was a student of W. H. Perkin, Jr. and O. Wallach and was Professor of Chemistry at Birmingham, 1925-1946.
- 3 Edmund Langley Hirst (1898-), student and associate of Sir Norman Haworth; since 1944 Professor of Chemistry at Edinburgh.
- 4 William F. Magie (1858-1943), professor of physics at Princeton University from 1890 to 1929.

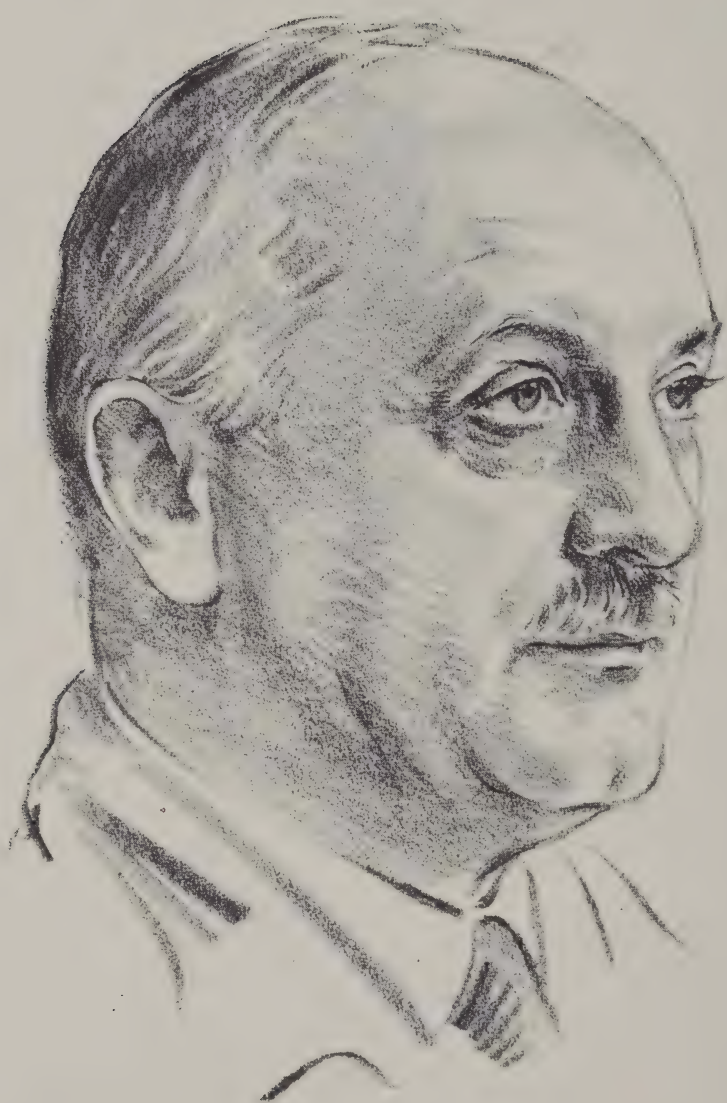
- 5 The change in optical rotation with time exhibited by a freshly prepared sugar solution.
- 6 Hermann Walther Nernst (1864–1941), Nobel laureate in chemistry, 1920; one of the founders of the science of chemical thermodynamics.
- 7 "Das Buch der Grossen Chemiker," Band II, G. Bugge, ed., Verlag Chemie, Berlin, 1930, p. 391 ff.
- 8 Anomers are stereoisomeric sugars differing only in the configuration of the reducing carbon (carbon 1 in formula I on p. 1537).
- 9 Arthur Becket Lamb (1880–1952), student of Arthur Michael and T. W. Richards, professor of chemistry, Harvard University, 1920–1948, and editor of the *Journal of the American Chemical Society*, 1917–1949.

MELVILLE L. WOLFROM

•• 111 ••

Ernst Späth

1886-1946



WHEN a second son was born on May 14, 1886, to the blacksmith Späth in the small village of Barn, in the Northern Silesian province of the Austro-Hungarian Empire, nobody expected that this boy was destined to become one of the leading organic chemists of our time. In line with the traditional custom, the limited family finances were used to allow for a higher education for the elder son, but the younger boy, Ernst, was to continue in his father's modest trade. Ernst inherited from his father an enormous energy which the village blacksmith Späth thought to be the right quality for success in his trade.

It was Ernst Späth's mother who recognized her son's love for learning and especially for the natural sciences. She persuaded her husband that their younger son should also be permitted a high school and college education. This meant that the family had to tighten the belt considerably to be able to bear the expenses; Ernst Späth never knew the word "plenty" throughout his whole period of education.

In his early high school years Ernst Späth was fortunate to have a teacher who instilled in him an interest in natural sciences—especially chemistry. Many years later, Ernst Späth used to speak gratefully to his friends and students about this teacher and the guidance he had received from him during the early period of his education. It was his good fortune to find another inspiring teacher later on, when he studied chemistry at Vienna University. This other teacher was Rudolf Wegscheider, who quickly discovered his student's abilities and helped guide him toward an academic career.

When Ernst Späth graduated with full honors from high school, he had proven to his parents that their efforts had not been wasted, and he was then allowed to continue his studies. His first goal was to become a high school teacher. Later, when he found support in his teacher Wegscheider, he quickly decided to devote himself to chemistry.

In order to facilitate the studies of his student, Rudolf Wegscheider offered him an assistantship at the Chemical Institute of Vienna University. The small income from this position allowed Ernst Späth to supplement the meager allowance which his parents were able to give him, but what was still more important, this first academic position determined the young man to seek the career of a college professor.

After obtaining his doctorate in 1910, he had to interrupt his professional career at the University of Vienna for military duty during World War I. Nevertheless, he was allowed to continue in a professional capacity at the laboratories of the university. Once the war was over, he returned to the academic career at the same university, and even though he had obtained several very tempting offers from a number of German universities, he decided to stay in his beloved Vienna. In 1917 he became a full-fledged member of the academic faculty of Vienna University in the field of chemistry; he advanced in 1921 to the title of assistant professor, in 1923 to professor and one year later, in 1924, he became *ordinarius* and head of the Second Chemical Institute. This opportunity arrived when his predecessor, Wilhelm Schlenk, went to the University of Berlin.

His untiring energy, his clear vision of the goal which he had set for himself, and his never-ending optimism served well in the building and expansion of the Second Chemical Institute and inspired his students and co-workers. The students working on their theses for the doctorate were especially privileged to have his help and attention. He gave them many hours of patient advice, and he also inspired them by his own research activity, his skill in all laboratory techniques, and the long hours which he devoted to research. It was not unusual for him to return in the evening to the laboratory and work into the early hours of the morning. His lectures were alive and inspiring. He did not use a written text to deliver them; instead, he spoke freely, supplementing his lecture with many demonstrations, and he always tried to adjust his teaching to the latest developments in chemistry. At the end of the lecture he was usually surrounded by students asking him many questions which he would patiently answer. These seminars

after the lecture would last nearly as long as the lecture itself and gave him the opportunity to pick the ablest among his audience and invite them to collaborate with him in his research studies. It was easy to notice how much he enjoyed the close contact with his students. In addition, he used to walk through the many laboratories of the Second Institute, stop and talk with his students and often remain for a considerable time at a student's work bench, advising him how to conduct the experiment, demonstrating proper techniques, and personally making adjustments to the apparatus in order to improve the experiment. In the many research projects which he conducted with the cooperation of his assistants and students, there was hardly a decisive experiment which he would not perform himself. Through his active participation in the experimental portion of each research project conducted by his group of collaborators and students, he made certain that in the final report the conclusions were based on exhaustive and accurate experimentation. Himself a master of the latest experimental techniques, he insisted that his students acquaint themselves with all of them. The temporary lack of a special piece of laboratory glassware was never a reason for him to stop the experiment. He was skilled in building or improvising the needed equipment. Often he demonstrated to his students his ability as a glass blower and taught them how to make and design their own equipment.

With his enormous capacity for work Späth was able simultaneously to conduct and supervise a number of research projects, deliver the lectures, devote considerable time to his younger students, and conduct the administration of a large institute in the most efficient manner. The administration of the Second Chemical Institute was accomplished with only a few clerical assistants.

At all times there were about twenty students working on their doctoral theses under his guidance and with his active and close collaboration. Many of them came from abroad. It was not unusual to hear several different languages spoken in this part of the institute. Racial or religious discrimination was foreign to Ernst Späth's thinking, and one could find there students of different races and creeds working side by side, getting acquainted, and developing friendship with one another. This happened at a

time when racial and religious discrimination was becoming extremely noticeable all over Central Europe and especially at the Central European universities. Once, when students from other sections of the university tried to invade the Second Chemical Institute in order to stage an anti-Semitic demonstration and to eject the Jewish students who were working there, the intruders were stopped by Ernst Späth and told that they had invaded a place of learning which had no use for their shallow ideologies. This personal courage was demonstrated later on repeated occasions when Späth used all his personal influence to protect colleagues and students who were exposed to the hatred of political extremists. Ernst Späth had no political affiliations. All of his energy was devoted to the service of humanity through his beloved chemistry at a time when some of his colleagues had lost their way from science and education and had surrendered the traditional liberalism of the university to violence and mob psychology.

Ernst Späth had started his chemical work as the student of the physical chemist Wegscheider, but he soon changed to organic chemistry. The chemistry of the natural plant substances became his special field of interest. According to his own statement, Späth made the decision to devote his research activity to the chemistry of the natural plant substances shortly after the conclusion of the First World War. In 1918, while spending a vacation on the beautiful Adriatic island of Brioni, he made a literature search of the alkaloids. Because of the important position of the alkaloids in pharmacology and their use in medicine, Späth earned for himself an international reputation by conducting brilliant and thorough research to establish the chemical configuration of these substances. There were two reasons for Ernst Späth's decision. Austria had become a very small country after the conclusion of the war in 1918. Its resources were very limited, and there was not much money in the budget of the university laboratory. Therefore, Späth had to choose a field of research which did not require large sums of money. The second reason was that the necessity to work with small quantities of the product he was investigating had a special attraction to him. The then usual, not too accurate methods of the organic chemist did not appeal to him. The order and tidiness of

not only the master's private laboratory, but also of the others in the Second Chemical Institute was characteristic of his personality. The exactness that was required in the research operations dealing with very small quantities led to many discoveries in chemical research methods which have since become valuable tools in fields other than alkaloid chemistry.

In the nineteenth century, Austrian chemists like Rochleder, Hlasiwetz, and Redtenbacher had pioneered in the research of the chemical constituents of plants and were able to show considerable achievements. Ernst Späth's predecessors at the Second Chemical Institute of Vienna University, Zdenko Skraup and Guido Goldschmiedt, were also interested in research on alkaloids. It was therefore tempting to Späth to resume the tradition, especially since this trend had been interrupted by his immediate predecessor Schlenk who had devoted his work to the theory of organic chemistry.

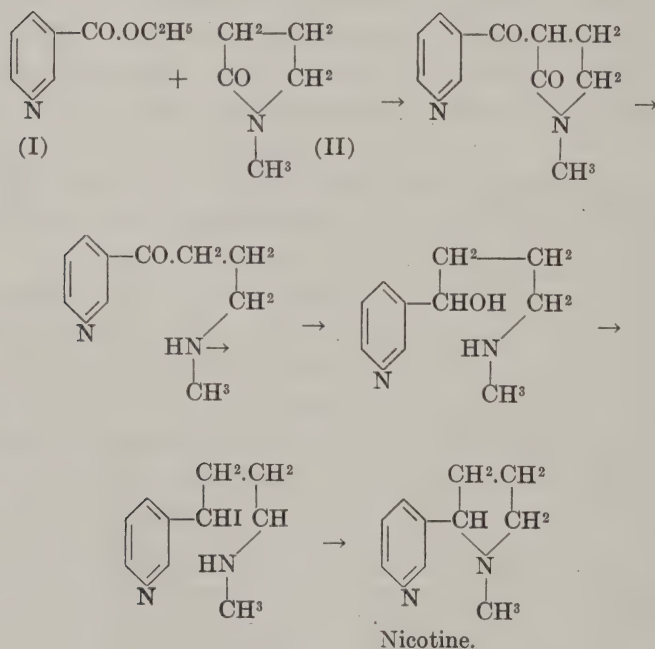
When Ernst Späth started his fruitful activity in alkaloid chemistry, there were still many questions unanswered, and there were several that also gave promise of financial success.

Although he was able to inspire many of the people around him, nevertheless some of them had to make a considerable effort to penetrate through the hard surface of this introvert personality in order to recognize his true nature. Some of his most brilliant students experienced this difficulty at the beginning of their contact with the master. It was then that Späth's deep sense of justice and discernment finally effected a mutual understanding.

There are 160 finished research projects in the field of alkaloids from Ernst Späth's laboratory. His first researches were devoted to the alkaloids belonging to the isoquinoline group to which ephedrine, papaverine, and others belong. He devoted work to the constituents of curare, to the chemical identity of chelidonine, the main alkaloid contained in the herb celandine (*Chelidonium Majus*), and to the alkaloids of the narcissus plants. Among the latter was tazettine whose chemical formula he ascertained. He also studied alkaloids contained in angotura bark, for instance, cusparine.

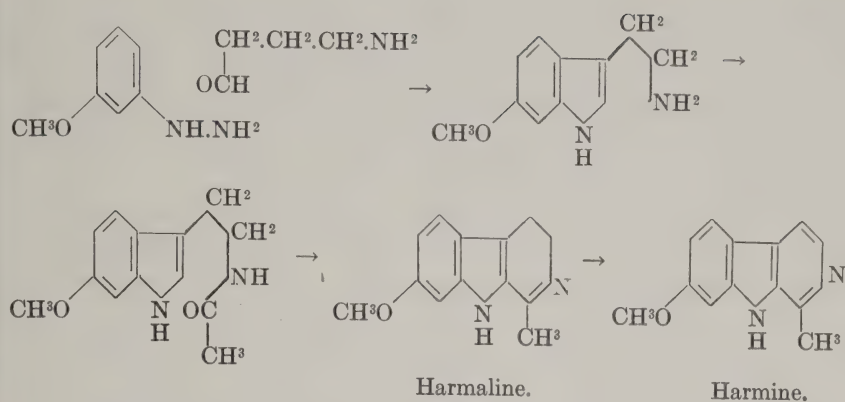
In many of his researches Späth tried to identify all the bases

contained in a drug; this procedure involved experimentally difficult work. Many of his results are of great importance in the field of plant physiology. Together with H. Bretschneider he developed a convincing synthesis of nicotine, and alone he proved the existence of a number of secondary alkaloids. He also described for the first time anabasine, nicotine, *N*-methylanabasine, and others. His thorough knowledge of the tobacco alkaloids is demonstrated in the monograph entitled "The Alkaloids of Tobacco" which he wrote with F. Kuffner.



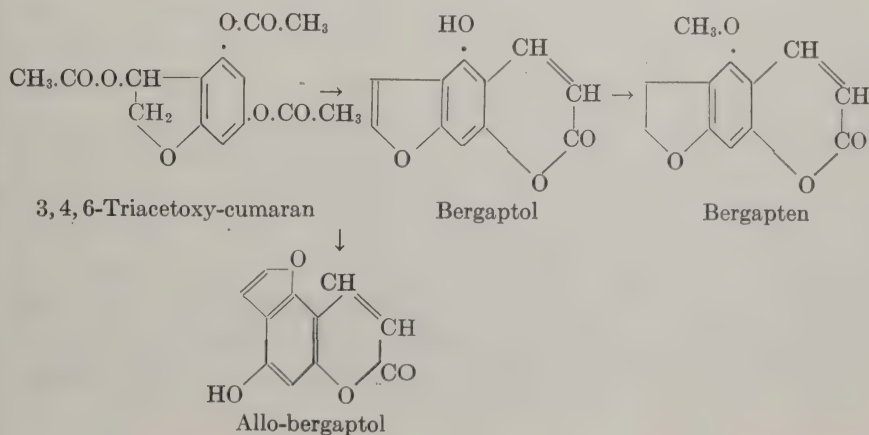
Späth's synthesis of nicotine¹ starting with the ethyl ester of nicotinic acid (I) and *N*-methylpyrrolidone (II)

Together with F. Galinowski he elucidated the chemical configuration of cytosine, the main alkaloid of *Laburnum Anagyroides* and other leguminous plants. Among other alkaloids which had attracted Späth's attention, one must mention harmaline because of the pharmacological importance of this drug in the treatment of influenza.



Späth's synthesis of harmine² starting with 3-methoxy-phenol hydrazine and gamma-aminobutyraldehyde

In the last fifteen years of his life, Späth devoted his scientific activity to another group of plant substances, the coumarins. More than sixty publications in this field witness his activity. His research started with a domestic Austrian plant from which Hlasiwetz had previously isolated pencedamine. Among other members of this group was khellin, which Späth isolated. This drug is interesting because of its pharmaceutical use in the treatment of asthma and angina pectoris. Späth's research on the coumarins is the foundation for the work that is being conducted at present and undoubtedly will be continued in the future because of the numerous derivatives which have significant physiological properties.

Späth's synthesis of bergapten³

Späth occasionally conducted other investigations dealing with natural products that belong to different chemical groups. Some of them are: cotoin, kynurenic acid, lactucin, podophyllotoxin, protocotoin, pseudobaptigenin, pseudobaptisin, saponins, and sparrasol. Among the methods he developed is the dehydrogenation of heterocyclic substances by using palladium.

During thirty years of an extensive scientific activity, Späth produced more than 300 major publications. The world recognized his genius by bestowing many honors upon him. In 1931 he became a member of the Carolinisch-Leopoldinische Academy for Natural Sciences in Halle, Germany; in 1934 he was elected to the corresponding membership of the Academia de Ciencias Exactas, Físicas y Naturales in Madrid; in 1937 he was awarded the nonresident membership of the Hungarian Academy in Budapest, and then he was made corresponding member of the Academy in Bologna, Italy.

From 1936, he was a member of the Comité d'Experts Scientifiques de l'Organisation de Cooperation Intellectuelle de la Société des Nations (Committee of Scientific Experts of the Organization for Intellectual Cooperation of the League of Nations). In 1937 he was elected an honorary member of the Associazione Italiana di Chimica and the Société de Chimie Industrielle of Paris.

The Vienna Academy of Sciences honored Späth in 1920 by awarding to him the Lieben Prize. In 1933 he was awarded the Lavoisier Medal of the Société Chimique de France and in 1937 the Liebig Medal of the Verein Deutscher Chemiker. In 1937 he was also given the Wilhelm Exner Medal of the Chamber of Commerce of Lower Austria.

Ernst Späth had very close ties with Vienna which he had adopted as his home and the site of his intellectual activity. When he was elected to the corresponding membership of the Academie der Wissenschaften in Wien (Vienna Academy of Sciences) in 1925, it was the fulfillment of his greatest ambition. In 1926 he became a full member of this venerable institution. Within the framework of the Vienna Academy of Sciences, Späth found the opportunity to honor his teacher Wegscheider. In 1929 he initiated and sponsored the Wegscheider Foundation on the occasion of the

seventieth anniversary of the great chemist who had started Ernst Späth on the path of chemical research. Späth devoted considerable effort and time in the service of the Vienna Academy, and in 1938 he was elected general secretary of the Mathematics and Natural Sciences Section of the Academy. One of his important achievements for the Academy was the enlargement of its library.

Ernst Späth possessed a profound love for his country, its science, and art. He had no use for political parties and their ideologies. The raucous year 1938 gave Späth the opportunity to become the champion of the persecuted, and he used his influence and the respect which he commanded to protect many of his colleagues whom he respected as scientists, but who had attracted the hatred of the ignorant and misled masses. At a time when Austria was at its most difficult position, impoverished and marred by the destruction of war, on October 30, 1945, he was elected president of the Vienna Academy of Sciences.

The re-establishment of the Vienna Academy is entirely his achievement. The old and venerable building which had housed this learned society was demolished by bombs during the war. It was Ernst Späth's achievement that the structure was rebuilt. He obtained the needed funds and, what was still harder, the building materials to do the job. His firm and quiet personality gained many friends and supporters among the members of the Austrian government, the military and civil authorities of the occupying powers, and many admirers abroad. His untiring efforts were crowned when he obtained the facilities of the Biological Station in Linz, Austria, from the Russians who occupied it.

On September 30, 1946, in Zurich, Switzerland, came the last act of the great scientist. He had come there as the delegate of the Vienna Academy of Sciences for the celebration of the two-hundredth anniversary of the Schweizer Naturforschende Gesellschaft (Swiss Society of Natural Sciences). Without any warning he succumbed that day to a heart attack. Only shortly before, he had celebrated his sixtieth birthday in the quiet of his home among his beloved family. This great and honest man, who was possessed by an untiring energy and love for science and his fellowmen, died quietly in the midst of his work and among his fellow scientists.

REFERENCES

Almanach Österr. Akad. Wiss., 97, 123, 304 (1947).
Österr. Chemiker-Z., 48, 57 (1947).

- 1 E. Späth, "Récentes synthèses d'alcaloides," *Bull. Soc. Chim.*, ser. 4, 53, 1379, 1933.
- 2 E. Späth, *loc. cit.*, p. 1383.
- 3 E. Späth, "Die natürlichen Cumarine," *Ber.*, 1937 A, p. 107.

ALFRED A. BACHER

.. 112 ..

Victor Moritz Goldschmidt

1888-1947



THE basic problem of geochemistry," said Victor Moritz Goldschmidt, "is to determine the quantitative chemical composition of the earth and to find the laws which underlie the frequency and distribution of the various elements in nature."

During the nineteenth and early twentieth centuries attempts were made, mainly by chemists, to collect the chemical and physical-chemical data relating to mineralogical and geological chemistry. In Switzerland, Schoenbein coined the name "geochemistry"; in Germany Carl Gustav Bischof published, between 1848 and 1854, his famous treatise on "Physical and Chemical Geology" which presented the chemical knowledge of his time. The great Berzelius in Sweden did much to elucidate the chemical genesis of minerals and rocks, and at the beginning of the century J. H. van't Hoff laid the foundation of the physical chemistry of salt minerals. The greatest contributions came from the work of the American petrologists F. W. Clarke and H. S. Washington. Modern geo-chemistry, however, had its origin in Oslo. The laws which determine the geochemical distribution of the elements were postulated by V. M. Goldschmidt from 1917 on.

Goldschmidt was born on January 27, 1888, in Zürich. His father, Heinrich Jacob Goldschmidt, was a distinguished physical chemist who came from Prague which was then, of course, part of the old Austro-Hungarian monarchy. His mother was Amelie Köhne, and Victor Moritz was their only child. In quick succession his father became professor in Amsterdam, then Heidelberg—where V.M. received his early schooling and in 1905 he was appointed professor of chemistry, succeeding Waage at the University of Oslo (then Christiania), at that time the only university in Norway. Famous for its tradition in the mathematical sciences, Oslo was also famous for its school in the earth sciences. V. M. matriculated in 1905 to study mineralogy, geology, inorganic and physical chemistry, and came under the inspiring influence of the great W. C. Brøgger, whom he soon equaled in the importance of his

geological and petrological work. Except for the winter terms of 1908 and 1911 when he worked under F. Becke in Vienna and P. von Groth in Munich, he finished his studies in Oslo and obtained his doctor's degree in 1911. After two years as a lecturer he was appointed, in 1914, at the early age of twenty-six, full professor and director of the Mineralogical Institute of the University of Oslo.

By then, shortly before the outbreak of World War I, the first scientific harvest was brought in. His earliest paper on the pyroluminescence of quartz¹ was published when he was a first-year student. The main work of this period, which has since become a classic, was his 480-page study on the contact metamorphism of the Oslo region² published in 1911. Throughout this monograph Goldschmidt applied physical-chemical considerations to geological problems, rightly regarding the whole planet earth as one single physicochemical system. It was perhaps the first time that, by Goldschmidt's mineralogical phase rule, the applications of Nernst's heat theorem and the law of mass action on complex systems of rocks mineralogy have come of age as an exact science.

It took Goldschmidt eight years to complete the fundamental investigations that followed his work on contact metamorphism: an intensive geological-petrographical study of regional metamorphism of the mountains of southern Norway.³

Long before war broke out the Goldschmidt family had become Norwegian citizens. When the general situation in the neutral countries deteriorated, and after the intensified U-boat warfare, Norway was largely cut off from overseas; sources of raw materials were badly needed. The result was that in 1917 the Norwegian government decided upon thorough research into the mineral resources of Norway, and entrusted Goldschmidt with this task. He became chairman of a Government Commission for Raw Materials and director of the Raw Materials Laboratory. This work, which was directed entirely toward practical ends during the war, was continued afterward along general lines from which developed a new branch of science, geochemistry, which from the theoretical and the practical point of view is of the greatest importance. Several schools of geochemistry existed already and a mass of material

was available. Apart from the American school, pre- and postwar Russia had produced some outstanding personalities such as W. J. Vernadsky, who did pioneer work notably in biogeochemistry, i.e., the frequency and distribution of elements in plants and animals. The work of today's leading expert on the origin of primitive life, Oparin, has its roots in Vernadsky's earlier work and is mainly a geochemical and biogeochemical complex of problems. There is also the school of the other leading Russian geochemist, A. E. Fersman, who died during the last war. Unfortunately his four-volume treatise on geochemistry has never been translated. However, the fundamental laws and principles underlying frequency and distribution of elements—the basic problem of geochemistry—were developed by V. M. Goldschmidt in Oslo between 1920 and 1928 and, when he was in Göttingen, by systematic research into the geochemistry of individual elements. That Russia alone has produced some 25,000 geochemists after the war gives some idea of the importance of modern geochemistry.

With an excellent team of co-workers, and with great energy, every conceivable method of chemical and physical analysis was used for the accumulation of data for a formidable task. Analytical methods had to be checked and adopted or new ones developed; carbon arc optical spectrography was developed; chemical analysis by characteristic x-ray spectra, already used by von Hevesy and by Assar Hadding in Sweden for geochemical purposes and mineral analysis, proved very useful; plans were also made by V. M. Goldschmidt for the construction of a mass spectrometer for the determination of the mass ratio of isotopes. The outbreak of the Second World War prevented Goldschmidt from introducing this instrument to geochemical research. Today mass spectroscopy has become a widely used tool in geochemical laboratories.

One of the methods extensively used by Goldschmidt was the analysis of crystal structure by x-rays, the great discovery of Max von Laue, and of W. H. and W. L. Bragg. The use of this method broadened the original views considerably, and almost as a by-product a new scientific discipline, crystal chemistry, was created.

One of the principal problems in the history of the earth that Goldschmidt approached is the partition of the chemical elements

during the geological evolution between gas and coexisting liquid phases, the subsequent crystallization of these liquid phases, of molten iron, iron sulfides, and fused silicates, and the distribution of the chemical constituents in these phases. According to their tendency to enter one or the other of these phases, the elements could be classified into siderophile (metal melt), chalcophile (sulfide melt) and lithophile groups (silicate melt). A fourth group, the atmophile group, includes those elements which in pregeological times differentiated into the primordial atmosphere. It is of great interest that the distribution of the chemical elements among the three phases (iron, sulfide, silicate) is closely related to their atomic volume and the structure of their electronic shells.

The main controlling factors during these stages of differentiation are the chemical affinities of the various elements toward oxygen and sulfur and their latent heat of vaporization as compared with the affinity of the most common terrestrial heavy metal, iron. Goldschmidt took as a measure of these affinities the free energy of oxidation per gram atom of oxygen of the lowest oxides of the electropositive elements and the corresponding data for their sulfur compounds. Elements which are extremely rare in the earth crust—the lithosphere—are gold, the elements of the platinum group, and also nickel, cobalt, and germanium. They can be expected in the iron phase, the siderosphere. On the other hand the alkali and alkali-earth elements, silicon, aluminum, titanium, elements with a higher free energy of oxidation than iron, will, in the primordial differentiation, have concentrated in the outer silicate crust of the earth. Incidentally, it is known that the siderophile elements—gold, platinum metals, etc.—enter fused iron and iron alloys and are thus found as by-products in iron and steel works. The other analogon in metallurgical practice is the concentration of lithophile elements in the slag.

The next step after the primordial differentiation is the cooling of our planet and the crystallization of the silicate crust, a process which is still going on in rock formation from volcanic magmas.

Goldschmidt attacked the problem of finding the general laws and principles of geochemistry "from the viewpoint of atomic physics and atomic chemistry and to find out the relationships be-

tween the geochemical distribution of the various elements and the measurable properties of their atoms and ions." He soon discovered that the principal factor regulating the entrance of atoms and ions and the distribution of the rarer elements in the crystalline phases of igneous and metamorphic rocks was the size of the atoms and ions and not their weight. During the gradual crystallization of liquid solutions, those atoms or ions of rare metals are caught in the already existing three-dimensional lattice which, because of their size, fit into this lattice. Those atoms and ions which are either too small or too big to be caught remain in the liquid. This idea led to the discovery of the fundamental relationship between crystal structure and chemical constitution:

The structure of a crystal is conditioned by the numerical proportions, the proportion of size and the properties of polarization of its ultimate particles, and not only the structure but also other important properties of crystals, such as hardness, solubility and melting temperature, could be predicted from the properties of the atoms, and so, in the course of our geochemical investigations, the foundations of modern crystal chemistry were laid. These relationships were not limited to crystalline phases, but applied as well to the properties of solidified glasses . . .

Until then crystallography was for the mineralogist and the practical chemist: as Goldschmidt wrote, "a purely descriptive auxiliary science which made possible the recognition and distinction of crystalline materials whether they were minerals or technical products." Goldschmidt with his excellent team of co-workers—T. F. W. Barth, G. Lunde, I. Oftedal, L. Thomassen, W. H. Zachariasen and others—embarked on a hitherto unsurpassed systematic series of x-ray studies. In 1926 the atomic and ionic sizes, i.e., the radii of the greater part of the chemical elements in their different stages of electrical charge or ionization, were determined. Goldschmidt was now in a position to predict in which minerals, rocks, or ores a certain element could be found—an achievement equally important scientifically and practically. To give only one example from innumerable cases which had been proved: Nickel

and magnesium have as divalent positive ions the same radius of 0.78 Å; this is the reason why nickel is found in magnesium silicates of igneous rocks, and the percentages of both follow each other closely. Goldschmidt could soon predict the sequence of fractionated crystallization, taking into account the electrostatic forces between the positive metal ions and the negative silicate ions.

However, there are additional forces which support the electrostatic attraction of the ions in the crystal frame work, i.e., van der Waals forces, polarization forces, and the electron pair forces. They result in a measurable contraction of the lattice which is highest in the case of nickel orthosilicate, followed by magnesium and then by iron (ionic radius = 0.83 Å). Nickel, in the fractionated crystallization from magmatic or other solutions, is the first, and iron the last to enter the mixed crystal. The concentration of nickel in magnesium-orthosilicate is sometimes of economic importance.

Goldschmidt could further predict the sequence of crystallization in cases of elements of the same size and practically the same ionic radius, but different electrical charge. If a divalent element, such as magnesium, is the main constituent in a crystal in contact with a saturated solution containing, as minor constituents, a trivalent element, such as scandium, and a monovalent, such as lithium, then, owing to the excess of electrostatic attraction, the trivalent scandium is preferentially built into the crystal—"captured"—whereas the univalent element lithium, owing to its smaller electrostatic charge, is only "admitted" to the lattice toward the end of the crystallization period. We understand now that scandium is not nearly as rare as it was formerly considered, but is a frequent constituent of many igneous rocks, especially magnesium silicates.

The problem of ionic substitution in minerals, which has occupied the mind of every mineralogist, was simply and elegantly solved by Goldschmidt's fundamental laws of crystal chemistry.

The chemical and geochemical behavior of elements with the same valency and almost the same ionic radii is of especial interest. The classical examples are the pairs aluminum/gallium and zirconium/hafnium. The trivalent gallium (radius = 0.57 Å) is "hidden" in aluminum (radius = 0.62 Å) and practically every

aluminum mineral, every bauxite contains up to 100 grams of gallium per ton of aluminum. It accompanies aluminum through all the stages of industrial manufacture, and can be detected in practically every aluminum alloy. The tetravalents zirconium and hafnium have the ionic radii $Zr = 0.87 \text{ \AA}$; $Hf \equiv 0.86 \text{ \AA}$. It will be remembered that in zirconium minerals von Hevesy discovered hafnium, the existence of which was predicted by Bohr's atomic theory. Goldschmidt called this hiding of a rare element in another "camouflage." The most famous example of camouflage is found in the rare earth elements, and the celebrated elucidation of the geochemical and chemical behavior of this fascinating group of elements, closely related to their ionic radii and valency, is one of the most magnificent achievements of Goldschmidt's work.

In his monumental work "Geochemische Verteilungsgesetze der Elemente, I-IX,"⁴ Goldschmidt laid down the fundamental laws of geochemistry and crystal chemistry. These 600 pages contain the life work of one who, more than anyone else, has laid in two branches of science the foundations on which later generations will build. Nos. I-VIII contain the result of his work in Oslo, IX (the "ninth symphony" as he used to call it) originated from one of his happiest periods of life in Göttingen. No. VII contains the famous laws of crystal chemistry and No. VIII the relations between the structure and properties of crystals. One of the problems Goldschmidt approached in the latter communication are the factors influencing the hardness of crystals. Based on earlier work by Reis and Zimmermann, and by Friedrich, Goldschmidt systematically—supported by hundreds of investigated substances—extended our knowledge by showing how the hardness of a crystal was determined by the interatomic distance, the valency, and the structure type. Goldschmidt, however, did not stop here and went on to the question of whether it is possible to "construct" crystals of certain well-defined and desired properties, such as hardness, melting point, solubility, optical refraction, chemical reactivity, etc. Unfortunately this work on "model structures" of crystallized silicates and silicate glasses has remained comparatively unknown in the English-speaking world, as it was published in a journal not easily accessible (*Zeitschr. für technische Physik*, 1927). In this paper,

readers will find the scientific basis of a problem of quite fundamental importance—how to construct solid materials of certain physical, chemical, and mechanical properties.

The year 1929 was a decisive year for V.M. (as he was affectionately called). In that year he was invited to join the faculty of natural sciences of Göttingen as full professor and head of the Mineralogical Institute. Other invitations from foreign universities had come to him, and more than one university was anxious to obtain the collaboration of the recognized leader in his field. Stockholm had previously tried before; V.M. decided in favor of Oslo. A few years before he went to Göttingen the University of Munich had planned to appoint V.M. to the vacant chair of Paul von Groth. The failure of this proposal is a typical and ominous sign of the political influence of a small group of professors in the town which later became the hotbed of Nazism. Unfortunately at the decisive meeting of the faculty a number of politically moderate and reliable people were absent, believing that Goldschmidt's appointment was already decided. As a result the invitation was turned down because "We already have one Jew at the Faculty." In protest against this racial discrimination, the "Jew at the Faculty" resigned. He was Richard Willstätter, Nobel Laureate, and one of the greatest organic chemists of his time.

In view of this experience, V.M. may have been reluctant to accept an invitation from another German university. However, Göttingen was not Munich and, in the tradition of its great permanent Under-Secretary Althoff, the Prussian Minister of Education, treated V.M. with the greatest courtesy and, fully aware of the great importance of this appointment, agreed to all V.M.'s wishes. It is said that after a meeting for Goldschmidt's official acceptance and final decisions the very dignified Under-Secretary and his advisers joined in a dance of joy.

Goldschmidt, with his father and their Norwegian housekeeper, Frökken Marie Brendigen (his mother had died shortly before), moved to Göttingen where V.M. bought a house in Wagnerstrasse. On arriving in Göttingen, father and son found the town "dressed over-all"—not to greet the distinguished scientist, but to honor Colonel Düsterberg, the leader of a somewhat nationalistic organi-

zation of soldiers called "Stahlhelm" (the Steel Helmet). The Stahlhelm was harmless compared with those organizations that replaced it after 1933; Colonel Düsterberg, being only "partly" Aryan, was forced by the Nazis and S.S. to resign. Nevertheless, it gave the Goldschmidts an ominous foretaste of things to come.

There was a galaxy of eminent men of science in Göttingen at that time. The mathematical tradition—uninterrupted from the days of Gauss—was carried on by David Hilbert, Courant, Landau, and others; the organic chemist and Nobel Laureate Wallach was living in retirement and his successor (also a Nobel Laureate), A. Windaus, of cholesterol fame, was at the height of his career. Another Nobel Prize winner was Zsigmondy; the physics department was headed by the triumvirate James Franck, Max Born, and W. Pohl—after 1933 the first two, both Nobel Laureates, became "unbearable." Prandtl, one of the founders of modern aerodynamics, was one of Göttingen's great men; so was G. Tammann, the physical chemist who was still very active after his retirement, and who was succeeded by A. Eucken. The zoologist Kühn and the astronomer Kienle became great personal friends of the Goldschmidts. There was also a young generation, many of whom have since become world-famous.

The few years before 1933 were perhaps the happiest in Goldschmidt's life. In Oslo he was something of a lone wolf; in Göttingen he not only inspired his own students and colleagues, but drew inspiration from them all—the physical chemists, the inorganic chemists, the physicists, astronomers, and biologists. It was an almost ideal cooperation among scientists of every branch, and nobody sat in an ivory tower, anxiously guarding the results of his own work from intruders. In addition there was a constant exchange of ideas with foreign visitors and guests.

The Mineralogical Institute was housed in a former school which was adapted according to V.M.'s requirements. One wing contained the lecture theater, students' working rooms and laboratories, and the teaching collections of crystals, minerals, and rocks. The teaching department was connected to the third-floor research wing by a wide corridor in which magnificent specimens of minerals were displayed. There, a group of young and very able scien-

tists set out under the direction and guidance of V.M. to study the geochemistry of individual elements. The laws which govern the distribution of elements were postulated in Oslo. They were now applied to the systematic survey of a large number of elements.

This period between 1929 and 1935 or, to be more precise, 1933, was the happiest epoch in the lives of V.M. and his aging father H.J. There the lonely man found not only devotion of his collaborators, which he had enjoyed in Oslo, but also the warm friendship and admiration of his colleagues.

In those pre-war days Goldschmidt was a heavily built, stout man, shy and often difficult to approach. He had an almost old-fashioned courtesy which could change to an outspoken but equally courteous frankness in scientific and other arguments. Shortly before he died he told me a story which is a clue to his strange personality. When his father moved to Heidelberg young V.M., who was about six years old, attended a private school. His mother had impressed upon him that he must always be polite and also tell the truth, however disagreeable. After a few days at his new school, the headmaster, a big man with a black beard and of alarming appearance, asked young V.M. how he liked the school, and ended by saying: "I hope we will become good friends. Do you already like me?" Aware of his mother's admonition, after a moment's pause V.M. replied: "Nicht so besonders, Herr Göckel" (not particularly, Sir).

As well as this "truthful politeness" which is found in some of his polemics and in many of the discussions after scientific meetings (not always to the delight of those concerned), he had a grim and sarcastic sense of humor, and was very quick-witted. In all scientific and personal affairs he was completely sincere, honest, and incorruptible. There was no room in his department for anyone who did not measure up to his own scientific and moral standards, nor for sloppy and untidy workers. He was enthusiastic about new, exciting, scientific results wherever they came from; but his criticism of unsound or too highly publicized work could be devastating. He had a certain naive streak of vanity, and he was easily hurt if insufficient credit was given to his work. I well remember his reaction to a long review article on some fundamental problems

of geochemistry by a well-known chemist, in which only one reference was given to a paper by V.M., and that, on a minor subject. However, this was after 1933 and the author had undergone a color metamorphosis to brown—the Nazi color. (It is only fair to emphasize that in the case of V.M.G. this was one of the rare exceptions. Almost all of his collaborators and colleagues stood by him in the dark days after 1933. Only one case is reported in which a younger and presumably ardent Nazi scientist dared to refer to V.M.'s name in the Nazi prescribed form—V.M. (Israel) Goldschmidt—in the Nazi-sponsored *Zeitschrift für die gesamte Naturforschung* (in the Germany of those days nicknamed “*Zeitschrift gegen die gesamte Naturforschung*”).

He was by nature a pessimist and, partly perhaps because of his Jewish origin and of the anti-semitism which he had experienced from his childhood on, he occasionally suffered from a feeling of persecution. This was why he did not readily trust people until he knew them well and also why he was so responsive to genuine overtures of friendship. His kindness and generosity were unfailing, even to people unknown to him personally. He was a real animal lover and his garden was almost a bird sanctuary. There is the story about his learning the cat language, an attempt which came to an abrupt stop when he was attacked by a large tomcat to whom he had, apparently, unwittingly been extremely rude. The household, in addition to its human inhabitants, consisted of the famous dachshund “Bazi”—which tyrannized father and son; three squirrels demanded and received a home in the bathroom, a toad hibernated in the cellar, and a family of bats resided in the loft. Each had a name; and the toad shared his with a well-known and not too endearing character in Göttingen. One of the squirrels was named Parsifal (“because he was indescribably stupid”) another was Richard (Weil er so stark riecht”), but the most notorious was Magdalena, who came to a sad and untimely end. V.M. gave a birthday party for Bazi and several dog guests were invited to share the birthday cake. In the excitement, Bazi concluded that on this special day everything was permitted and ended the feast by devouring Magdalena.

Only a few of his devoted assistants and collaborators in Göt-

tingen can be mentioned—most of them are today heads of university departments: F. Laves, Zurich; Th. Ernst, Erlangen; H. Hauptmann, São Paulo; W. v. Engelhardt, Tübingen; H. Witte, Darmstadt; R. Mannkopff, Göttingen; C. Peters, Vienna.

The scientific harvest of this short Göttingen period was particularly rich. From 1930 to 1935 Goldschmidt published an inspiring series of papers on the geochemistry of rarer elements. In each case terrestrial material from all parts of the world was analyzed; meteoritic matter was also included. New analytical methods were developed, such as the cathode layer technique which proved to be one of the most valuable methods for the detection of elements down to and below 0.01 per cent. It is impossible to condense into a few paragraphs the results of well over two dozen papers, dealing with the geochemistry of the alkali metals, nickel, the noble metals, germanium, gallium, scandium, boron, arsenic, and selenium. In almost every case the abundance of the elements in the earth's crust, in meteorites, and in stellar atmospheres were investigated. One typical example is the investigation by V.M. of the geochemistry of germanium and its occurrence—with other rare elements—in coal and coal ashes.

This element is distributed in silicates of the upper lithosphere, owing to the similarity of the ionic radii of Ge and Si. It is also present in iron meteorites, and Goldschmidt found striking concentrations of it in the ashes of certain coals. A preliminary spectrographic analysis of the ashes of the boiler in V.M.'s institute and the soot in the chimney led to a systematic investigation of the geochemistry of coal ash. The highest amount—1.6 per cent GeO_2 —was found by V.M. in ash from samples of Northumberland coal. Still higher amounts (up to 9 per cent) were found later in lignites from the District of Columbia, and in certain Russian coals.

The biochemical, or rather biophysical, mechanism of the enrichment of this and other rare elements—boron, arsenic, beryllium, cobalt, nickel, platinum metals—is still far from clear and needs further elucidation. Among those elements most highly concentrated in coal ash is arsenic. V.M. thought that one of the causes of the professional disease of chimney sweeps, skin cancer, may be the high content of arsenic in soot and flue dusts. It should

be noted that petroleum shows a still greater affinity for trace elements than coal, and certain ashes of petroleum are used as a vanadium ore containing up to 70 per cent V_2O_5 .

Some thirty years ago the metallurgy and the industrial uses of minor elements were practically unknown. It did not "pay" to recover rare elements or to develop industrial uses for these. Today, thirteen years after Goldschmidt's death, some of the minor elements have become of the utmost industrial importance. Goldschmidt showed where to find them and laid the foundation of their geochemical and crystal-chemical behavior.

The peaceful lives of Goldschmidt, father and son, were fundamentally changed and their work interrupted in 1933. The "thousand years" of the Third Reich had begun. Monsieur François Poncet, French Ambassador in Berlin, summed it up "C'est la victoire des Boches sur les Allemands." Göttingen and the other German centers of learning were systematically destroyed by the Nazis. Many eminent scientists deeply regretted this—but they did not protest, or make a firm stand against the measures taken by the Nazis against science and the arts. Some of V.M.'s students went to Berlin in the hope of convincing the Ministry of Education that V.M. must remain in Göttingen. Goldschmidt and his father, who had not previously belonged to any faith, ostentatiously joined the small Jewish community in Göttingen. V.M. was determined, in the interests of his students, to continue his work at the University as long as he could, knowing that soon he too would be dismissed and forced to leave the country. He became more lonely and withdrawn than before, constantly careful not to "compromise" or endanger his non-Jewish friends and colleagues. His sense of humor became more grim than ever. His father was once perturbed at being greeted by someone with "Heil Hitler." Goldschmidt retaliated by remarking that surely no atheist could be offended if greeted by "Grüss Gott."

He continued to work on his extensive research program; early each morning and again until late each night he sat at his ancient double-keyboard typewriter, writing scores of letters to colleagues and friends abroad, recommending young scientists who had lost their positions for racial reasons. Many young scientists owe to

V.M. not only their careers in countries outside Germany, but even their lives.

In 1935, after a new wave of anti-Semitism, Goldschmidt resigned his chair and returned to Norway. The Norwegian citizenship which he had to resign when he went to Göttingen was immediately granted and a chair at Oslo University offered to him. The Goldschmidts arrived back in Norway almost penniless; although emigrants and refugees from Germany were allowed to take their personal belongings with them, the money allowed was only ten marks per person. Much later part of Goldschmidt's money was transferred to Oslo as the result of a very courageous and outspoken letter written by F. K. Drescher-Kaden, V.M.'s successor in Göttingen, to the president of the German Reichsbank, Hjalmar Schacht. The house in Wagnerstrasse and all his other possessions were lost without compensation from Germany.

He rented the top floor of a small house in Holmenkollen, and divided all his energies between his scientific work and helping refugees from Germany and the countries invaded by the Germans before the war. He wrote the ninth and final publication of the "Verteilungsgesetze", a book of 150 pages covering the abundance and distribution of the individual elements and atomic species, and geochemical and cosmochemical data; in this attempt to estimate the mineral mass ratios of the chemical elements he also included isotopes, thus laying the foundation stone of isotope geology. He resumed his work for the Norwegian Raw Materials Laboratory, assisted by his devoted collaborator Aslak Kvalheim (who later became his successor in this government laboratory), and he continued his geochemical research. As a side line, and a money-making hobby, he resumed the industrial work he had done after World War I, when he did so much to develop the utilization of Norwegian raw materials. On the west coast of Norway there are large deposits of olivine; Goldschmidt discovered that it has refractory properties, and he himself developed the methods successfully used in industrial furnaces and ceramic kilns of transforming olivine rock into industrial refractories. In addition he made use of olivine sand and crushed dunite rocks instead of quartz sand for making molds for foundries. The olivine molds not only produce

excellent castings of steel and high-melting ferro-alloys, but also reduce, and may even eliminate, the danger of silicosis in foundries.

In the tranquility of his new home Goldschmidt was at peace again, although he was distressed by tension and oppression in Germany and anxious about many of his friends still living there. His correspondence was greater than ever, and the file marked "N.A." (non-Aryan) grew daily. A personal tragedy for him was the sudden death of his father, and he became more lonely and withdrawn than before. Future and worse developments in the political theatre, however, soon made him realize that death had spared his father from participation in the coming cataclysm.

I went to stay with him in Oslo shortly after his father's death. He had aged, his health had deteriorated, and he was embittered and tired. But he went on with his scientific and his relief work with almost inexhaustible energy. He spent more than he could afford on helping other people and managed to bring an aged aunt and a niece—still a child—from Germany to Oslo, and the niece from there to the U.S.A. He still enjoyed his food and an occasional drink and he maintained his old-fashioned courtesy. His humor had become more whimsical, more grim, and sometimes even caustic. I remember one day when I asked him to come with me to take some flowers to the crematorium as a tribute to his parents. We stood reverently in front of the urns, all made of beautiful green Norwegian olivine, two with the ashes of his parents and a third, empty and destined to hold his own, and finally V.M. remarked dryly: "Ja, ja, the whole family in magnesium orthosilicate."

His pessimism in those pre-war days was sometimes almost unbearable. He knew the omens and foresaw the coming pandemonium from which there was no escape, and yet he worked and made plans for further research. The spectrographic unit was in full swing, and plans were ready for a new mass spectrometer with which to study the abundance and distribution of isotopes. And then war broke out, bringing the darkest days of Goldschmidt's life. He had always been a man of strong likes and dislikes and could not always see eye-to-eye with his colleagues. During the war, and especially when Norway was overrun by the

Germans, he forgot all his animosities in a personal attempt to resist the waves of evil which swept over Europe. He kept in touch with those friends in Germany who still dared to write to him and, in order not to compromise them during censorship, signed his letters illegibly. His main correspondence was with English friends; even during the Nazi occupation many messages reached the Allies through Goldschmidt's help.

By nature timid and anxious, he grew in stature during the war years, but his health suffered. Finally he was arrested by the S.S., his property was confiscated and he was sent to one of the concentration camps which the new masters had installed. These camps were full of the Norwegian intelligentsia—university teachers, lawyers, writers, etc.—regarded as dangerous by the regime. It is true, and it should never be forgotten, that nearly everyone in Norway was engaged in the resistance. Goldschmidt's case, however, was a special one: in addition to being one of the most prominent Norwegians, he was also a Jew, and therefore earmarked for extermination in the gas chamber. In November, 1942, he was listed for deportation to Poland, but at the last moment, probably through the clever intervention of the Norwegian police, and owing to his poor health, he was temporarily released. Then, with the help of the Norwegian resistance he was smuggled across the Swedish frontier in a load of hay which some German soldiers prodded with a fork.

Goldschmidt did not stay long in Sweden. He was eager to offer his services to the Allies, and in the spring of 1943 he was brought to England. It was in this country, and especially in Scotland, that, although seriously ill, he felt at peace again. Under the auspices of the Agricultural Research Council he first went to Craigiebuckler, near Aberdeen, to work at the Macaulay Institute for Soil Research. He was warmly received by its director, Dr. (now Sir) William Ogg and his wife, and for the first time in many years he knew what it meant to live in a free country. He took a great interest in soil research and, when Ogg became director of Rothamsted Experimental Station, he moved with him to Harpenden. He was liked by everybody and soon affectionately called "Goldie"; he took the greatest interest in the Institute's work on

trace element distribution, and used to remark that it was in England, and through his contacts with Dr. Ogg, Dr. Alex Muir, and others that he began "to understand what geochemistry really is"—put with great modesty, this was certainly a great appreciation of the excellent work of British soil chemists.

Goldschmidt always hated the writing of papers and books, and he used to tell his pupils in Göttingen to write their papers as concisely as a Scotsman would if they were to be sent by telegram. It was with difficulty that Dr. Ogg and his colleagues eventually persuaded V.M. to write his last magnum opus, and gave him every facility for his work. But the task was too great and his health already too seriously undermined. Seven hundred folios were written, but he could not finish the rest. The ultimate book "Geochemistry" was completed after years of hard work by Alex Muir with the collaboration of A. Kvalheim and published posthumously by O.U.P. in 1954.

Many honors came to Goldschmidt—he received an honorary degree at Aberdeen University, and also the highest award of the Geological Society, the Wollaston Medal; but nothing pleased him more than his election, as one of its fifty foreign members, to the Royal Society, London. Perhaps, had he lived longer, he would have received a Nobel Prize, which he so richly deserved. His deepest satisfaction, however, was the kindness he received, and the fact of his freedom—in Göttingen, when one Nazi riot followed another, he and his father carried hydrocyanic acid in a capsule for emergency use as a final evasion of Nazi cruelty. In Norway, too, during the occupation, he carried poison in his pocket. On one occasion a university colleague of his in Oslo asked Goldschmidt for a capsule. "This poison," answered V.M., "is for professors of chemistry only. You, as professor of mechanics will have to use the rope." This was the typical grim humor of Goldschmidt. In England he did not need the poison any longer, and in a gay ceremony at Rothamsted it was solemnly buried deep in the garden.

I saw Goldschmidt again in January, 1946, after a long interval, and found him greatly changed in appearance. From then on I went to Harpenden once or twice every week to spend the day

with him. His agonizing experiences in Norway and his recent illnesses had made him lose weight and he looked more like a pathetic survivor of a Nazi concentration camp. In spirit, however, he was indestructible; he was still easily hurt if somebody failed to give credit to his work and he suffered, often with justification, from a sense of persecution. His English, although grammatically correct and even fluent, was known as "Goldschmidt English" because of his quaint pronunciation. As usual he was more generous than his means really allowed and the pockets of his suits, which always became baggy, bulged with dozens of small pieces of paper: notes of atomic constants, old bills, bus tickets, and the addresses of people to whom he wished to write, or whom he wished to help in their academic career.

In one fundamental way he had changed: the bitterness had gone—he no longer hated those who, in so grim a way, had twice interrupted his work, undermined his health, and shortened his life. One episode influenced V.M. deeply and occupied his mind until the end of his life: it happened early in November, 1942, in the County Hospital in Tönsberg, Norway, which was then the internment camp for Norwegian Jews. After a day of humiliation and torment by his Nazi jailers, V.M. talked to two other prisoners, whose names deserve to be recorded: Moses Katz, an orthodox Jew and a hosiery peddler, and Lesser Rosenblum, socialist, atheist, and manufacturer of umbrella handles. V.M. suggested that they should remember the names of their tormentors, so that any survivors might exact retribution. The reply of the pious Moses Katz was a surprise to V.M.: "Revenge is not for us; that must be left to the Almighty." With the arrogance of a scientist confident of his superior knowledge, V.M. asked what prayers would be permissible to God from men in their position. Katz replied without hesitating a moment: "You may pray that the hearts of your enemies may be enlightened." Goldschmidt, still not admitting defeat, turned to the atheist Rosenblum and asked for his view. His reproof was equally unexpected: "We must break the evil circle of retribution, or there can never be an end to evil."

Goldschmidt became very humble after this experience. He had escaped, but his two friends from Tönsberg were facing death in

Poland's gas chambers. He regarded their sayings as lucid and practical improvements on the Old Testament. Through them he learned not to forget, but to forgive.

The prolonged strain he had undergone, his escape, and the frequent adjustments to new countries and languages and people had completely undermined V.M.'s health, and for weeks he had to stay in bed. On one occasion he was staying with the Oggs. Dr. Ogg, on his way to bed very late, heard groans coming from V.M.'s bedroom. He had had a heart attack and was convinced that he was dying. Between groans he kept saying "This is the end. I have done my best for Norway and Britain." A doctor was called at once and Goldschmidt was given oxygen; but his condition was critical and the doctor, scarcely expecting him to live until the morning, gave Dr. Ogg the name and telephone number of an undertaker. V.M. appeared to be unconscious but evidently heard these remarks. He had enormous will power and was not yet prepared to be defeated by illness. When he was being carried out to the ambulance in the morning he was joking about the undertaker.

His mind worked constantly; many fascinating theories occupied him and were developed in talks with visiting friends. No record of these is available as Goldschmidt never committed to paper, or published, ideas which he could not yet prove. He strongly disliked the premature publication of theories: "Make two thousand experiments, and then you have your theory and can publish both," he used to say.

However, he did write two papers which, for different reasons, he was unwilling to publish. There exists a handwritten manuscript, "Geochemical Aspects of the Origin of Complex Organic Molecules on the Earth as Precursors to Organic Life." It was published after his death in a series of popular scientific books but has remained practically unknown to scientists, and Goldschmidt himself would never have agreed to its publication in its unfinished form. Some of the ideas expressed in this draft may one day reappear and their significance be recognized.

The second paper—actually more a note—was written in co-operation with G. Nagelschmidt and was never published because Goldschmidt felt it was, perhaps, undignified to end his funda-

mental scientific work with a note on album Graecum (dog feces), a prosaic and unattractive product, however interesting in its chemistry, in which insoluble phosphates are transformed into white and soluble ones. It may be recalled that before World War I it was used in the manufacture of fine, high-grade leather. The idea of this note must have come to V.M. during the war, when he grew vegetables in a small suburban garden outside Oslo where many people kept dogs. Album Graecum is an ideal phosphate fertilizer for a poor soil; but if it would be undignified as a scientific paper V.M. thought it would be even more undignified for a middle-aged professor to collect album Graecum from suburban pavements for his garden. He was in any case a very reluctant gardener, and had a widely representative collection of weeds in his allotment.

For several months in Harpenden, when he was too weak to leave his bed, he must have felt that his life was slowly drawing toward its close. He did not speak of the disappointments, the sorrows, the pains, and the dangers he had experienced, but of bygone and happy days; of Göttingen and his friends and pupils who resumed contact with him after the war. He was happy that his old Institute had two of his friends as his successors, first F. K. Drescher-Kaden and after him C. W. Correns; and he was happy that his work was carried on by the younger generation which had been so strongly influenced by him. In his weakness V.M., who had never spoken German since 1939, sometimes lapsed unconsciously into his mother tongue. It was a moving experience to visit Goldschmidt in those days—the lonely man with some enemies, but with many devoted friends. These he remembered in gratitude, the others he forgot. "Should you see Dr. Lonsdale or Professor Tilley, and if you write to my old friend Eskola, please remember me to them," he would say, wanting them all to know that he was still alive. He could no longer go to see the Oggs, but they came and looked after him and he kept his friendship and gratitude for them until he died.

However, his time had not yet come. He recovered sufficiently to prepare for his return to Oslo. Once he felt better, his unfailing will power took possession of him, and he made plans to resume his scientific work on a large scale. At the end of June, 1946, he left England and arrived safely in Oslo. "Father's Return" was

celebrated enthusiastically at the Raw Material Research Laboratory, and he was delighted to see among other friends W. Zachariasen of Chicago University, one of the pupils of whom he was most proud. At his flat much of his furniture had been recovered with the help of the government, and there were letters from Göttingen, offering him his old chair and from China, inviting him to organize raw materials research in that country. Soon, however, he had to undergo examination and treatment in several hospitals. His reports were optimistic, heart, kidneys, and lungs seemed to be satisfactory, and he hoped to have several years ahead in which he could work, provided he "followed the recognized principles of Moses Katz." Miss Brendigen had again joined his household, and had provided him with what he regarded as a delicious specialty, fresh whale meat! In October for the first time he mentioned a black spot on his leg; he received x-ray treatment, but the growth proved to be malignant and required surgery. The carcinoma could not be removed completely, and again Goldschmidt had to go into the hospital. Still he continued working on his book, directing scientific and industrial research and writing letters to his friends. In March, 1947, he entered the surgical ward for the sixth operation. On March 19 I had a few scribbled lines that the operation had been successful and that he would be allowed to go home on the following morning. He arrived home on the twentieth, complained of a sudden intense pain in his head, and died almost immediately.

In one of his last letters to me he wrote:

The wisdom of the Moses Katz principles is undeniable. . . . And I am fully convinced that it is my duty towards science and decency to stand firm in continuing my work as long as health permits, thus giving an example to at least some of my junior colleagues. Often I think that (to maintain these principles) to be even more important than my contributions to scientific and industrial research and my scientific teaching. To set a new standard of morality is a matter of great urgency in these times . . .

NOTES AND REFERENCES

- 1 "Die Pyroluminescenz des Quarzes," *Kgl: Norske vidensk.-skab. Selskabs. Skrifter*, No. 5, 1-15 (1906).

- 2 "Die Kontaktmetamorphose im Kristiania-Gebiete," *Ibid.*, No. 1, 1-483 (1911).
- 3 "Geologisch-petrographische Studien im Hochgebirge des suedlichen Norwegens. I-V" *Ibid.* (1912, 1915, 1916, 1920).
- 4 "Geochemische Verteilungsgesetze der Elemente. I-IX," *Ibid.* (1923-1937).

ACKNOWLEDGMENTS

I gratefully acknowledge the help and advice of friends of V. M. Goldschmidt: Professor C. W. Correns, Göttingen; Dr. Alex Muir, Harpenden; Sir William Ogg, Edzell, Angus; Professor C. E. Tilley, F.R.S., Cambridge.

PAUL ROSBAUD

.. 113 ..

Thomas Midgley, Jr.

1889-1944



THOMAS MIDGLEY, JR., discovered a new tool for chemical research: with its aid he invented two new, very important industrial chemicals. Twice he set out deliberately to put together a new chemical compound with exact specifications for its chemical and physical properties, intended to do a very particular job. His synthesis of the antiknock agent, tetraethyl lead, and the refrigerant, trichlorofluoromethane, now used also as an aerosol propellant, were beautiful pieces of pure, or at least deliberately planned chemical research. Midgley is memorable for the new, time-saving idea he introduced into modern research techniques.

There was a rich strain of inventiveness in his blood. His mother's father, James Emerson, invented the insert-tooth saw. His own father made half a dozen notable inventions.

Thomas, Sr., born in London in 1860, came to the United States with his parents as a small boy and received his education in the public schools of Worcester, Massachusetts. In 1874 he got a job in a shoe factory and four years later, at eighteen, he was a foreman in a wire-drawing plant. In 1884 he moved to Beaver Falls, Pennsylvania, as superintendent of the Hartford Steel Company, and it was here that Thomas, Jr., was born on May 18, 1889.

When his son was a year old, Thomas Midgley ventured into his own business, making wire-goods specialties, but in 1896 he became factory manager of the Columbus Bicycle Company, Columbus, Ohio. Again, four years later, he began on his own to manufacture steel wire wheels for bicycles and automobiles. In 1905 the father was back in New England as consultant to the Hartford Rubber Works and Morgan & Wright. In 1914 he launched the Midgley Tires Company in West Virginia, but soon moved to Ohio. Here he was joined by his son, who had been graduated three years before from Cornell.

The father held many patents in wire-drawing, in specialties made from wire, and in rubber-compounding. His various business ventures were based upon his own inventions, notably a woven wire wheel with detachable tires, which was replaced by the more popular "clincher" tires, and the Midgley collapsible core tire,

which had the advantage of being quite puncture-proof, but it never supplanted the pneumatic tube which, at this time, was being rapidly improved.

Young Tom Midgley was sent to Betts Academy at Greenwich, Connecticut, a small private school with a superior faculty. Among his teachers was a former professor at the Naval Academy, Annapolis, who gave him his first instruction in chemistry and with whom he long remembered an argument on the periodic table. This sophomoric debate on God *vs.* the tiny particles was a forecast of the novel application he was to make years later of Mendeleev's periodic law. But when he entered Cornell, Tom elected, not chemistry or chemical engineering, but mechanical engineering, in which he received his M.E. in 1908 and his Ph.D. in 1911.

Without tarrying for graduation exercises and his diploma, he hurried to Dayton, Ohio, to report on his first job in the Inventions Department of the National Cash Register Company. For the compelling reason that he was very much in love with a young lady just graduating at Ohio Wesleyan, he wanted to get on the payroll as quickly as possible. Within two months, on August 3, 1911, he and Carrie M. Reynolds of Delaware, Ohio, were married. As he said, "Like all good fairy tales, we lived happily ever afterwards." They had two children; a son, Thomas III, and a daughter, Jane, who became Mrs. Edward Z. Lewis.

Research and development work at the National Cash Register Company was then presided over by Dr. Charles F. Kettering, and Midgley later acknowledged that "it was his dynamic personality; a bigger salary than anyone but an optimist could hope I could possibly earn; and the Ohio address of National Cash, that made me choose this job—but mostly it was Boss Kett."

Kettering handsomely returned the compliment. More than once he said, "The greatest discovery I ever made was Tom Midgley."

Certainly it was the influence of Boss Kett that brought him back to Dayton from his association with his father in the Midgley Tires Company. Meanwhile, Kettering had set up the Dayton Engineering Laboratory (Delco) to develop his own inventions. Among these was a home lighting system for which he had modified the regular internal combustion engine to use kerosene because at that time many cities had fire laws forbidding the storage of

gasoline in residential property. The kerosene-fueled engine developed such a bad knock that it occasionally cracked the cylinder head. Midgley, who was working on battery hydrometers, was assigned the job of finding the cause of knocking and how it might be eliminated.

He arranged a series of optical lenses to magnify and record the shape of the pressure wave which soon indicated that the knock was not caused by preignition, as had been supposed, but was due to the rapid rise in pressure after ignition and near top dead center. Kettering suggested that kerosene dyed red might absorb radiant heat and so vaporize more quickly and run more smoothly.

Had Midgley been a good physicist he would have recognized that this hypothesis was not workable, but as an experimentalist he went to the laboratory stockroom for an oil-soluble red dye. Finding none, at the suggestion of Fred L. Chase, he used iodine. The knocking stopped. They tried a dozen different red dyes, to find a cheaper reagent, but none eliminated the knock. When they found that colorless ethyl iodide was a capital antiknock agent, it was clear that iodine, not color, stopped the knock. Thus Midgley at once discovered by chance the first antiknock and identified scientifically the cause of this phenomenon. He patented the Midgley High Speed Indicator, which won him the Longstreth Medal of the Franklin Institute.

These researches turned Midgley into a chemist. Realizing his shortcomings in chemistry, he began a stiff course of self-education. For the next three years, given a few free moments, he was to be found deep in some stout chemical text and he acquired the habit of buttonholing his chemical associates to ask them very pointed questions.

We were in the midst of World War I: better aviation gas was a sore need. Collaborating with the Bureau of Mines, the Dayton laboratory staff attacked the antiknock problem under Midgley's leadership. He tackled this job with all his celebrated gusto backed by do-or-die determination. He had plenty of expert help: Alan R. Albright, T. A. Boyd, Carrol A. Hochwald, and Charles A. Thomas, all of the Delco group, later Robert E. Wilson and Charles S. Venable, then both professors at M.I.T.; finally Charles M. A. Stine, Willis Harrington, Elmer K. Bolton, and others from Du

Pont, to name but a few of the many whose advice and assistance Midgley time and again acknowledged gratefully. They went to work by the good old Edisonian method: "Try everything on the laboratory shelf and if nothing works make up some new ones."

From the front lines a cable reported that captured German aviation gas contained cyclohexane; Midgley and three associates worked one night through, attempting to hydrogenate benzene. Leo Baekeland, who was assisting the Army in this frantic fuel hunt, skeptically offered a wooden medal for the first pint of cyclohexane, which was actually produced at Dayton, October 26, 1917, using nickel oxide as a catalyst with a yield of 23 per cent. Tests showed that while the freezing point of cyclohexane is 40°F., a mixture of 80 per cent cyclohexane and 20 per cent benzene did not freeze till -40°. By July a pilot plant, built by Boyd, produced 50 gallons, and a liter bottle in a plush-lined mahogany case was sent to Baekeland. Plant experience nearly doubled the yield and flying tests modified the mixture to two-thirds cyclohexane and one-third benzene. Christened Hecter, this additive made it possible to increase the compression of an aviation engine from 5.5:1 to 8:1. The war ended before the 500-gallon-a-day cyclohexane plant was completed.

The cut-and-dry search continued. "From melted butter and camphor to ethyl acetate and aluminum chloride" was how Midgley ruefully described these tests, "and most of them had no more effect than spitting in the Great Lakes."

Hydrogen peroxide had the distinction of being the first positive knock-promoter found and zinc ethyl the first metallic alkyl tested. On January 30, 1919, it was discovered that two cubic centimeters of aniline was a more effective antiknock than a gram of iodine. This was the first tangible encouragement. It came at the right time, for the war was over, and it was agreed that after the turn of the year "this wild goose chase should be abandoned." So the hunt went on, and during the following summer two college professors—McPhearson of Ohio State and Ebaugh of Denison—brought down suitcases full of different chemicals for trial.

March 1, 1920, the Dayton Laboratory was taken over by General Motors. Splendidly housed in the former Dayton-Wright airplane factory, they received general instructions to continue the

antiknock work and raise the sights to include carbon-dissolving compounds and the broad problem of more, better, and cheaper motor fuel.

The hawk-eyed Kettering picked up in a newspaper item that selenium oxychloride had been hailed as a "universal solvent," and at his suggestion Midgley very skeptically tried this out. By many experiments both chlorine and oxygen had been classified as elements that generally increase knocking, but the selenium compound was a capital antiknock agent. Simultaneous tests with sulfur oxychloride demonstrated that it was a splendid knock promoter. This chemical contradiction arrested Midgley's attention. Hochwald prepared diethyl, methyl, propyl, and phenyl selenium and the corresponding tellurium compounds. All proved to be more or less successful antiknock additives to gasoline.

To this hint Midgley's inventive brain responded immediately. He was disgusted with the slow, wasteful, hit-and-miss procedure. Why not narrow the field by an investigation of compounds based upon the periodic arrangement of the elements?

This was the germ of Midgley's new, time-saving research technique. He used a special arrangement of the elements by Robert E. Wilson, based on Irving Langmuir's theory of atomic structure. This new approach suggested a study of the metallo-organic compounds, and in four months Midgley demonstrated indubitably that antiknocking is a periodic function of the elements and highest as one went down the table.

Tetraethyl tin having proved exceptionally effective, on December 9, 1921, Midgley and Hochwald prepared tetraethyl lead. They tested 1/40 of 1 per cent of it in kerosene and it gave better results than 1.3 per cent of aniline, their adopted standard. The long hunt, started in July, 1917, for a satisfactory antiknocking agent had ended.

Midgley played an important supporting role in the commercial development of ethyl gas. The primary problem was an economical, large-scale manufacturing process. It was solved by a combination of methods devised by Midgley, the Du Pont and the Standard Oil of New Jersey research staffs. This led to the joint organization of Ethyl Corporation of which he was vice-president, and at the beginning, general manager. Initial formation of lead oxide and its

deposition on valves was cured by the addition of ethylene dibromide. This created a demand for far more tons of bromine than had ever been dreamed of, which prompted the recovery of bromine from the sea according to a process suggested by Midgley, but perfected naturally enough by the Dow Chemical people. Since 1892 this company had been the largest American producer of bromine, extracted from Michigan brine. Another jointly owned company, the Ethyl-Dow Corporation, opened its famous bromine-from-seawater plant at Kure Beach, North Carolina, in 1934.

Amid these industrial developments, Dr. Lester S. Keilholtz, chief engineer of the Frigidaire Division of General Motors, came to Dayton with a message from Kettering. Artificial refrigeration was blossoming luxuriantly. Ammonia was still the great industrial refrigerant: methyl chloride and sulfur dioxide were the leading rivals in the household field. A disastrous accident in a Cleveland hospital dramatically emphasized the poisonous character of the former and the American Medical Association took pains to point out that sulfur dioxide (used in the early Frigidaire machines) was not less dangerous. A number of bad-smelling warning additives to the refrigerants were suggested and made obligatory by state and municipal health ordinances. But Kettering, keenly apprehending all the implications of this situation, was not satisfied with a warning.

"We must have," he said to Midgley through Keilholtz, "a non-toxic, nonflammable, cheap refrigerating agent, quick! What can you do about it?"

Here was a challenge with definite specifications—nontoxicity and nonflammability—but also with rigid limitations, for the much-needed chemical must have a boiling point between 0° and -40°C .

While waiting to join Midgley and the Frigidaire envoy at lunch, Albert L. Henne and Robert McNary went to the library; they checked the International Critical Tables of volatile organic compounds, and noted the obvious mistake that recorded the boiling point of carbon tetrafluoride as -15°C . Discussion of this error over coffee focused attention on fluorine compounds, possibly chlorofluorides, and the probability that the chemical they sought would be a reasonably complex compound.

Midgley thought of the periodic table arranged according to the Langmuir theory of atomic structure which had so profitably narrowed the antiknock search. It was quickly found that only elements on the right side with vacant spaces were volatile; that flammability is reduced from left to right; that toxicity declines from the heavy toward the light elements. Midgley himself has described what followed:

Plotting boiling points, hunting toxicity data, corrections; slide rules and log paper, eraser dirt and pencil shavings, all the rest of the paraphernalia that take the place of tea leaves and crystal spheres in the life of the scientific clairvoyant were brought into play.

By this paper-and-pencil research they concluded the most likely fluorine compound, probably the simplest to produce in quantity, was dichlorodifluoromethane. This seemed an unlikely selection. Chlorine and fluorine are highly toxic and the flammability of methane is almost notorious. But its physical properties as a refrigerant were perfect, and they began to check its toxicity.

In the preparation of this new refrigerant they had used five one-ounce bottles of antimony trifluoride, purchased through a laboratory supply house which had scoured the country for this tiny stock. Selecting one of these bottles at random, a few grams of the first Freon was prepared for trial. A guinea pig under a bell jar with a sample was not even irritated, but scampered merrily about most contentedly.

A second batch was prepared from another bottle. It killed guinea pig Number Two almost instantly. Something was radically wrong—but what?

Before making the third batch from a third bottle, Midgley applied the good old nose test. The unmistakable odor of phosgene revealed the trouble. Four of those five little bottles contained antimony trifluoride contaminated with a double salt-containing water of crystallization. This was enough to produce phosgene in ample quantity to be lethal. A simple caustic wash cleared this grave difficulty.

"The chances were four to one against us," said Midgley afterward, "and I often wonder if the sudden decrease of our first

guinea pig would not have so completely shaken our confident expectation that our new compound could not possibly be toxic, that—well, I still wonder if we would have been smart enough to have continued the investigation. Even if we had, the chances were still three to one against our using the one pure sample. I still wonder.”

This sensationally successful research was completed in three days, quick enough to astonish everyone connected with it. It was a striking demonstration of the time-saving possible by applying Midgley's new technique in attacking the problem of a new synthesis. His method, with all sorts of modifications, has since been applied to every kind of hitherto unknown compounds for many purposes—from lubricant antioxidants and synthetic detergents to insecticides and medicinals.

With a frank disclosure of his new method, Midgley announced the new product at the Atlanta meeting of the American Chemical Society, April, 1930. Several years later, when he was awarded the Perkin Medal, he gave a striking demonstration of its salient properties. Before that distinguished and dignified audience he breathed in a great gulp of Freon and then exhaled it through a rubber tube under a bell jar where it quickly extinguished a lighted candle. Here was proof positive that Freon was neither poisonous nor flammable. It was also a fine example of his instinct for the dramatic, his inborn sense of clever showmanship.

Tom Midgley was a jovial man. His good spirits fairly bubbled over. He was an outgoing man, fond of all sorts of people, a human being with such a relish for life that he had fun performing the most routine and monotonous tasks. Beneath this almost Pickwickian exterior was a keenly analytical intelligence, ambition to excel, and a dogged determination. He was as capable as he was popular, which, on both counts, is high praise.

Few chemists have won more awards for their accomplishments: the Nichols Medal, 1923; the Longstreth Medal, 1925; the Perkin Medal, 1937; the Priestley Medal, 1941; the Willard Gibbs Medal, 1942. But no other chemist had so many honors that were also personal tributes. He was elected president of the American Chemical Society and was named American delegate to the International Congress of Applied Chemistry and a member of the National

Academy of Science. Significantly, he was honored with membership in an exceptional number of professional fraternities: Sigma Xi, Phi Kappa Phi, Tau Beta Phi, Alpha Chi Sigma, and Atmos.

His death was tragic and untimely, for although crippled by an attack of polio in 1940, he was mentally active and busied with chemical affairs. He had devised a harness with pulleys to aid himself in arising from bed, and somehow he became entangled in it and was strangled. He died at his home in Worthington, Ohio, near Columbus, November 2, 1944, at the age of fifty-five.

NOTES AND REFERENCES

Midgley was granted 117 U.S. patents and was a prolific contributor to technical and scientific journals so that his professional career is well documented.

Robt. E. Wilson's presentation address of the Perkin Medal [*Ind. Eng. Chem.*, 29, 239 (1937)] and his informal sketch in *Ethyl News*, February 1948, are outstanding; see also "Who Was Who," II, 371.

For tetraethyl lead development, a full account, based on unpublished reports in files of General Motors Corp. with complete documentation, is in Williams Haynes, "American Chemical Industry," Van Nostrand, New York, 1945-54, vol. IV, pp. 396-405; also Kettering, *Trans. Soc. Automotive Engrs.*, 4, 269 (1919); H. S. Tegner, *Petrol. Times*, 19, 750 (1928).

For Freon: *Chem. Met. Eng.*, 37, 261, 286 (1930); *Ind. Eng. Chem.*, 22, 542 (1930); Haynes, *op. cit.*, V, 181-85.

For Ethyl Corp., *Ibid.*, VI, 151. For Thos. Midgley, Sr., *India Rubber World*, 62, 676 (1920).

Obits, *Chem. Ind.*, 55, 806 (1944); *Chem. Eng. News*, Nov. 10, 1944; *Rubber Age*, 56, 202 (1944); *New York Times*, Nov. 3, 1944.

WILLIAMS HAYNES

.. 114 ..

Wallace Hume Carothers

1896-1937



WALLACE HUME CAROTHERS, who died on April 29, 1937, was born in Burlington, Iowa, on April 27, 1896. His contributions to organic chemistry were recognized as outstanding and, in spite of the relatively short span of time for his productive accomplishments, he became a leader in his field with an enviable international reputation.

His paternal forbears were of Scotch origin and settled in Pennsylvania in prerevolutionary days. They were farmers and artisans. His father, Ira Hume Carothers, who was born in 1869 on a farm in Illinois, taught country school at the age of 19. Later he entered the field of commercial education and for forty-five years has been engaged in that type of work as teacher and vice-president in the Capital City Commerical College, Des Moines, Iowa. Wallace Hume Carothers was the first scientist in the family.

His maternal ancestors were of Scotch-Irish stock and were also, for the most part, farmers and artisans. They were great lovers of music, and this may account for the intense interest in and appreciation of music which Carothers possessed. His mother, who was Mary Evalina McMullin of Burlington, Iowa, exerted a powerful influence and guidance in the earlier years of his life.

To his sister Isobel (Mrs. Isobel Carothers Berolzheimer), of radio fame as Lu in the trio Clara, Lu and Em, he was especially devoted. Her death in January 1936, was a staggering shock to him and he was never able to reconcile himself completely to her loss.

On February 21, 1936, he married Helen Everett Sweetman of Wilmington, Delaware. Her father is Willard Sweetman, an accountant, and her mother, Bertha Everett. The family is of English-Welsh descent. Mrs. Carothers received her bachelor's degree in chemistry at the University of Delaware in 1933 and was employed in the patent division of the chemical department of the Du Pont Company from 1933 to 1936. A daughter, Jane, was born November 27, 1937.

Wallace was the oldest of four children. His education began

in the public schools of Des Moines, Iowa, to which city his parents moved when he was five years of age. In 1914 he graduated from the North High School. As a growing boy he had zest for work as well as play. He enjoyed tools and mechanical things and spent much time in experimenting. His school work was characterized by thoroughness and his high school classmates testify that when he was called upon to recite his answers revealed careful preparation. It was his habit to leave no task unfinished or done in a careless manner. To begin a task was to complete it.

He entered the Capital City Commerical College in the fall of 1914 and graduated in the accountancy and secretarial curriculum in July 1915, taking considerably less time than the average. He entered Tarkio College, Tarkio, Missouri, in September 1915, to pursue a scientific course, and simultaneously accepted a position as assistant in the Commercial Department. He continued in this capacity for two years and then was made an assistant in English, although he had specialized in chemistry from the time he entered college. During World War I the head of the department of chemistry, Dr. Arthur M. Pardee, was called to another institution, and Tarkio College found it impossible to secure a fully equipped teacher of chemistry. Carothers, who previously had taken all of the chemistry courses offered, was appointed to take over the instruction. Since he was rejected as a soldier on account of a slight physical defect, he was free to serve in this capacity during his junior and senior years. It is interesting that during his senior year there were four senior chemistry-major students in his class and every one of them later completed work for the doctorate, studying in the universities of this country and abroad. Today they bear testimony to the fact that as undergraduates they owed much to the inspiration and leadership of Carothers. •

Upon entering college his interest in chemistry and physical sciences was immediate and lasting, and he rapidly outdistanced his classmates in accomplishment. As a student he showed mature judgment and was always regarded by his fellow students as an exceptional person. Invariably he was the brightest student in the class regardless of the subject. Financial necessity required that he earn a large portion of his educational expenses. He always found time, however, to associate with the other students, though he

showed little interest for the boisterous enthusiasms of the average underclassman. During his last two years in college he was entrusted with a number of student offices to which he gave freely of his time and energy.

Leaving Tarkio College in 1920 with his bachelor of science degree, he enrolled in the chemistry department of the University of Illinois where he completed the requirements for the master of arts degree in the summer of 1921. His former instructor at Tarkio College, then head of the chemistry department at the University of South Dakota, desired a young instructor to handle courses in analytical and physical chemistry and was fortunate in securing Carothers for this position during the school year, 1921-1922. He went to South Dakota only with the intention of securing sufficient funds to enable him to complete his graduate work, but the careful and adequate preparation of his courses, as well as his care of the students under his direction, showed that he could be a very successful teacher of chemistry. He was still the same quiet, methodical worker and scholar, not forceful as a lecturer, but careful and systematic in his contact with the students. He always required adequate preparation of assigned work and was able to get a large volume in student accomplishment.

Simultaneously with his teaching work he started to develop some independent research problems. He was especially interested in the 1916 paper of Irving Langmuir on valence electrons and desired to investigate some of the implications it held in organic chemistry. Pursuing this idea he carried out laboratory studies which were reported in his first independent contribution to the *Journal of the American Chemical Society*, "The Isosterism of Phenyl Isocyanate and Diazobenzene-Imide." His second independent paper, published while still a student, was that on "The Double Bond." In this he presented the first clear, definite application of the electronic theory to organic chemistry on a workable basis. He described the electronic characteristics of the double bond and in essence included in his discussion everything that has since been written on this particular subject.

It was evident, even at this stage of his career, that teaching was not his forte. Literally he spent all of his spare time on research problems in which he became interested. A number of his newly

found friends in South Dakota tried to induce him to relax somewhat from his constant and sustained application to work, but without avail. He appeared to be driven by the many things that occurred to him as worthy of investigation in the laboratory.

He returned to the University of Illinois in 1922 to complete his studies for the degree of doctor of philosophy, which he received in 1924. His major work was in organic chemistry with a thesis under the direction of Dr. Roger Adams, on the catalytic reduction of aldehydes with platinum-oxide platinum-black and on the effect of promoters and poisons on this catalyst in the reduction of various organic compounds. His minors were physical chemistry and mathematics. He exhibited the same brilliance in all of his courses and in research which characterized his earlier accomplishments. Although specializing in organic chemistry, he was considered by the physical chemists to have a more comprehensive knowledge of physical chemistry than any of the students majoring in that field. During 1920-1921 he held an assistantship for one semester in inorganic chemistry and for one semester in organic chemistry. He was a research assistant during 1922-1923, and during 1923-1924 held the Carr Fellowship, the highest award offered at that time by the department of chemistry at Illinois. During these two years his seminar reports demonstrated his wide grasp of chemical subjects. The frequency with which his student colleagues sought his advice and help was indicative of his outstanding ability. At graduation he was considered by the staff as one of the most brilliant students who had ever been awarded the doctor's degree. A vacancy on the staff of the chemistry department of the University of Illinois made it possible to appoint him as an instructor in organic chemistry in the fall of 1924. In this capacity he continued with unusual success for two years, teaching qualitative organic analysis and two organic laboratory courses, one for premedical students and the other for chemists.

Harvard University, in 1926, was in need of an instructor in organic chemistry. After carefully surveying the available candidates from the various universities of the country, Carothers was selected. In this new position he taught during the first year a course in experimental organic chemistry and an advanced course in structural chemistry, and during the second year he gave the

lectures and laboratory instruction in elementary organic chemistry.

President James B. Conant, of Harvard University, was professor of organic chemistry at the time that Carothers was instructor. He says of him:

Dr. Carothers' stay at Harvard was all too short. In the brief space of time during which he was a member of the chemistry department, he greatly impressed both his colleagues and the students. He presented elementary organic chemistry to a large class with distinction. Although he was always loath to speak in public even at scientific meetings, his diffidence seemed to disappear in the classroom. His lectures were well ordered, interesting, and enthusiastically received by a body of students only few of whom planned to make chemistry a career. In his research, Dr. Carothers showed even at this time that high degree of originality which marked his later work. He was never content to follow the beaten track or to accept the usual interpretations of organic reactions. His first thinking about polymerization and the structure of substances of high molecular weight began while he was at Harvard. His resignation from the faculty to accept an important position in the research laboratory of the Du Pont Company was Harvard's loss but chemistry's gain. Under the new conditions at Wilmington, he had facilities for carrying on his research on a scale that would be difficult or impossible to duplicate in most university laboratories. Those of us in academic life, however, always cherished the hope that some day he would return to university work. In his death, academic chemistry, quite as much as industrial chemistry, has suffered a severe loss.

In 1928 the Du Pont Company had completed plans to embark on a new program of fundamental research at their central laboratory, the Experimental Station at Wilmington, Delaware. Carothers was selected to head the research in organic chemistry. The decision to leave his academic position was a difficult one. The new place demanded only research and offered the opportunity of trained research men as assistants. This overbalanced the freedom of university life and he accepted. From then on until his death his accomplishments were numerous and significant. He had the rare quality of recognizing the significant points in each problem

he undertook, and unusual ability for presenting his results in a most explicit and precise way, which led to clarity and understanding. In these nine years he made several major contributions to the theory of organic chemistry and discoveries which led to materials of significant commercial importance. Dr. Elmer K. Bolton, Chemical Director of the Du Pont Company, writes concerning Carothers:

At the time the Du Pont Company embarked upon its program of fundamental research in organic chemistry in the Chemical Department, Dr. Carothers was selected to direct this activity, because he had received the highest recommendations from Harvard University and the University of Illinois, and was considered to have unusual potentiality for future development. There was placed under his direction a small group of excellently trained chemists to work on problems of his own selection. The results of his work, extending over a period of nine years, have been of outstanding scientific interest and have been considered of great value to the Company as they have laid the foundation for several basically new developments of commercial importance.

In our association with Dr. Carothers, we were always impressed by the breadth and depth of his knowledge. He not only provided inspiration and guidance to men under his immediate direction, but gave freely of his knowledge to the chemists of the department engaged in applied research. In addition, he was a brilliant experimentalist. Regarding his personal characteristics, he was modest, unassuming to a fault, most uncomplaining, a tireless worker—deeply absorbed in his work, and was greatly respected by his associates. He suffered, however, from a nervous condition which in his later years was reflected in poor health and which became progressively worse in spite of the best medical advice and care, and the untiring efforts of his friends and associates. His death has been a great loss to chemistry and particularly to the Chemical Department. In my judgment, he was one of the most brilliant organic chemists ever employed by the Du Pont Company.

His reputation spread rapidly; his advice was sought continually, not only by his colleagues but also by chemists throughout the world. In 1929 he was elected associate editor of the *Journal of the American Chemical Society*; in 1930 he became an editor of *Or-*

ganic Syntheses. He took an active part in the meetings of the organic division of the American Chemical Society. He was invited frequently to speak before various chemical groups. He addressed the Johns Hopkins summer colloquium in 1935 on "Polymers and the Theory of Polymerization." That year he also spoke on the same subject before the Faraday Society in London, when his paper was considered one of the outstanding presentations on the program. His achievements were recognized by his election to the National Academy of Sciences in 1936—the first organic chemist associated with industry to be elected to that organization. During these years, from 1928 to 1937, several attractive academic positions were offered him but he chose to remain to the end with the company which had given him his opportunity for accomplishment.

Very early in life he displayed a love for books. From the time when *Gulliver's Travels* interest a boy on through Mark Twain's books, *Life of Edison*, and on up to the masters of English literature, he was a great reader. He possessed a singing voice that might have developed under training into something very worthwhile. Though he had no technical training in music, he was a lover of the great masters, and possessed a large and much-used collection of phonograph records of their works. He said occasionally that were he to start over he would devote his life to music.

Carothers was deeply emotional, generous and modest. He had a lovable personality. Although generally silent in a group of people, he was a brilliant conversationalist when with a single individual, and quickly displayed his broad education, his wide fund of information on all problems of current life, and his critical analysis of politics, labor problems and business, as well as of music, art, and philosophy. With all his fine physique he had an extremely sensitive nature and suffered from periods of depression which grew more pronounced as he grew older, despite the best efforts of his friends and medical advisors.

SCIENTIFIC WORK

His early scientific work involved an extension to organic compounds of Langmuir's idea of isosterism. He demonstrated that it was valid in the case of phenyl isocyanate and azoimide. Reactions

of the double bond were interpreted in terms of the electronic theory, using a point of view that has since gained wide acceptance.

His next efforts were devoted to demonstrating that any idea of "negativity" alone is inherently incapable of accounting for the relative reactivity of organic halides. He measured the base strength of a series of amines. His work on the thermal decomposition of alkali alkyls threw light on the inherent properties of the simplest organic anions.

The first field of which he was in a position to make an exhaustive study was that of acetylene polymers and their derivatives. With vinylacetylene and divinylacetylene made available to him, he completed a detailed study of these substances. It was his discovery that it was possible to add hydrogen chloride to monovinylacetylene with formation of 2-chloro-1, 3-butadiene, called chloroprene. This substance is analogous structurally to isoprene but polymerizes several hundreds of times more rapidly and leads to a product much superior to all previously known synthetic rubbers. It was the first synthetic material to show rubber's curious property of developing fibrous orientation when stretched and instantly reverting to the amorphous condition when released from stress. In resistance to aliphatic hydrocarbons and to most chemical reagents it is definitely superior to natural rubber. It has, moreover, a greater resistance than rubber to corona and sunlight. Carothers' work laid the foundation for the development by other chemists and by chemical engineers of the Du Pont Company of the commercial product which has found wide industrial use and which is marketed as neoprene.

These practical results, however, were of no greater importance than the theoretical. In the course of the investigation, many analogs and homologs of chloroprene were prepared and studied. Their behavior threw light on the relationship between the chemical structure of a diene and its suitability as a precursor of rubber. Fundamental information concerning the character and formation of the various polymers from these compounds was revealed and their structures clarified. The reactivity of the vinylacetylenes and the mechanism by which the products formed was studied in detail. New light was thrown on 1,4 addition and on α,γ rearrange-

ments. His work in this field was a basic contribution to acetylene chemistry.

The most outstanding scientific accomplishment of Carothers was his work on linear polymers. In a letter written to Dr. John R. Johnson of Cornell University on February 14, 1928, Carothers made a statement which demonstrated the careful thought and study which he had given previously to polymerization and polymeric molecules. It follows:

One of the problems which I am going to start work on has to do with substances of high molecular weight. I want to attack this problem from the synthetic side. One part would be to synthesize compounds of high molecular weight and known constitution. It would seem quite possible to beat Fischer's record of 4200. It would be a satisfaction to do this, and facilities will soon be available here for studying such substances with the newest and most powerful tools.

Another phase of the problem will be to study the action of substances xAx on yBy where A and B are divalent radicals and x and y are functional groups capable of reacting with each other. Where A and B are quite short, such reactions lead to simple rings of which many have been synthesized by this method. Where they are long, formation of small rings is not possible. Hence reaction must result either in large rings or endless chains. It may be possible to find out which reaction occurs. In any event the reactions will lead to the formation of substances of high molecular weight and containing known linkages. For starting materials will be needed as many dibasic fatty acids as can be got, glycols, diamines, etc. If you know of any new sources of compounds of these types I should be glad to hear about them.

These initial ideas culminated in the publication of a series of thirty-one papers in the field of polymerization. In these he proposed a general theory of condensation-polymerization and a logical and systematic terminology suitable for use in this previously disorganized field. The implications of his theory were illustrated by a series of experimental studies dealing with polyesters, hydrocarbons, polyamides, and polyanhydrides. These studies provided

experimental material for correlating chemical structure and physical properties of materials of high molecular weight, and furnished evidence favoring a view now generally accepted for the structure of such natural high polymers as cellulose. In these investigations a new technique—molecular distillation—was applied to the propagation of chemical reactions.

In this study a method new in principle was developed for the synthesis of many-membered cyclic compounds. A large number of many-membered cyclic compounds was synthesized, including several of entirely new types. Some of these compounds had musk-like odors and are otherwise similar in their properties to the genuine musks. One of these new many-membered ring compounds has found industrial application. The large amount of experimental material made possible important deductions bearing on the relationship between chemical structure and ease of ring formation. His contribution was a major one to the field of many-membered ring compounds, which is one of growing significance in organic chemistry.

He investigated the means by which polymers structurally analogous to cellulose and silk could be prepared, and synthesized a large number. These materials constituted the first completely synthetic fibres with a degree of strength, orientation, and pliability comparable with natural fibres. Their study made possible the development of a theory for the relation between structure, fibrous properties, and other physical properties. The work was brilliant and the most important aid in recent years to the understanding of such polymers. This information, and the modification of the physical and chemical properties of polymers by slight changes in the mode of preparation, has made possible the exploration of a wide variety of substances of most promising industrial application.

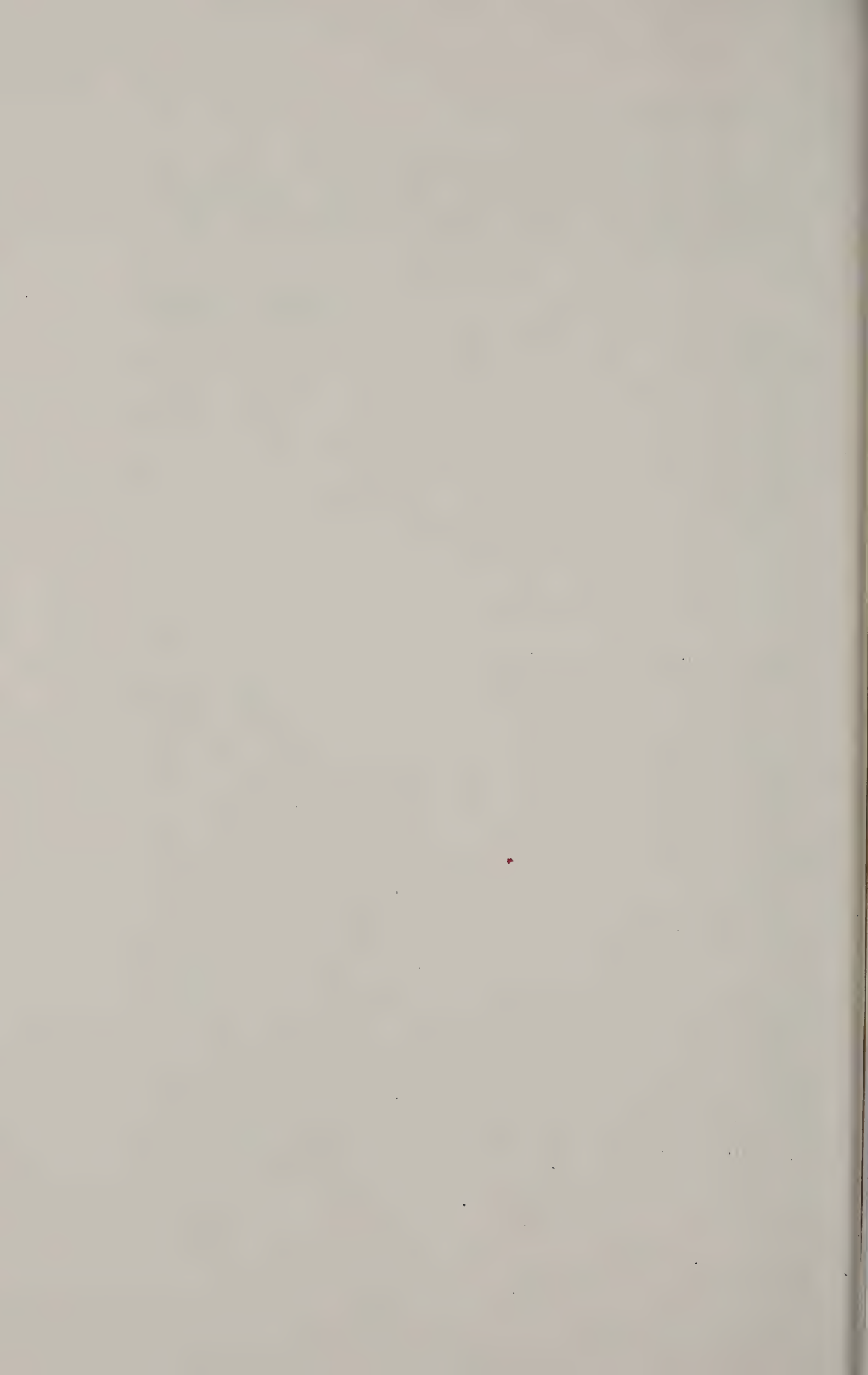
Based on this work, nylon was developed by the Du Pont Company. This consists of a synthetic fibre-forming polymeric amide with a protein-like chemical structure, characterized by extreme toughness, strength and peculiar ability to be formed into fibres and into various shapes such as bristles and sheets. Filaments of extreme fineness can be spun, much finer than the filaments of either silk or rayon.

WALLACE HUME CAROTHERS

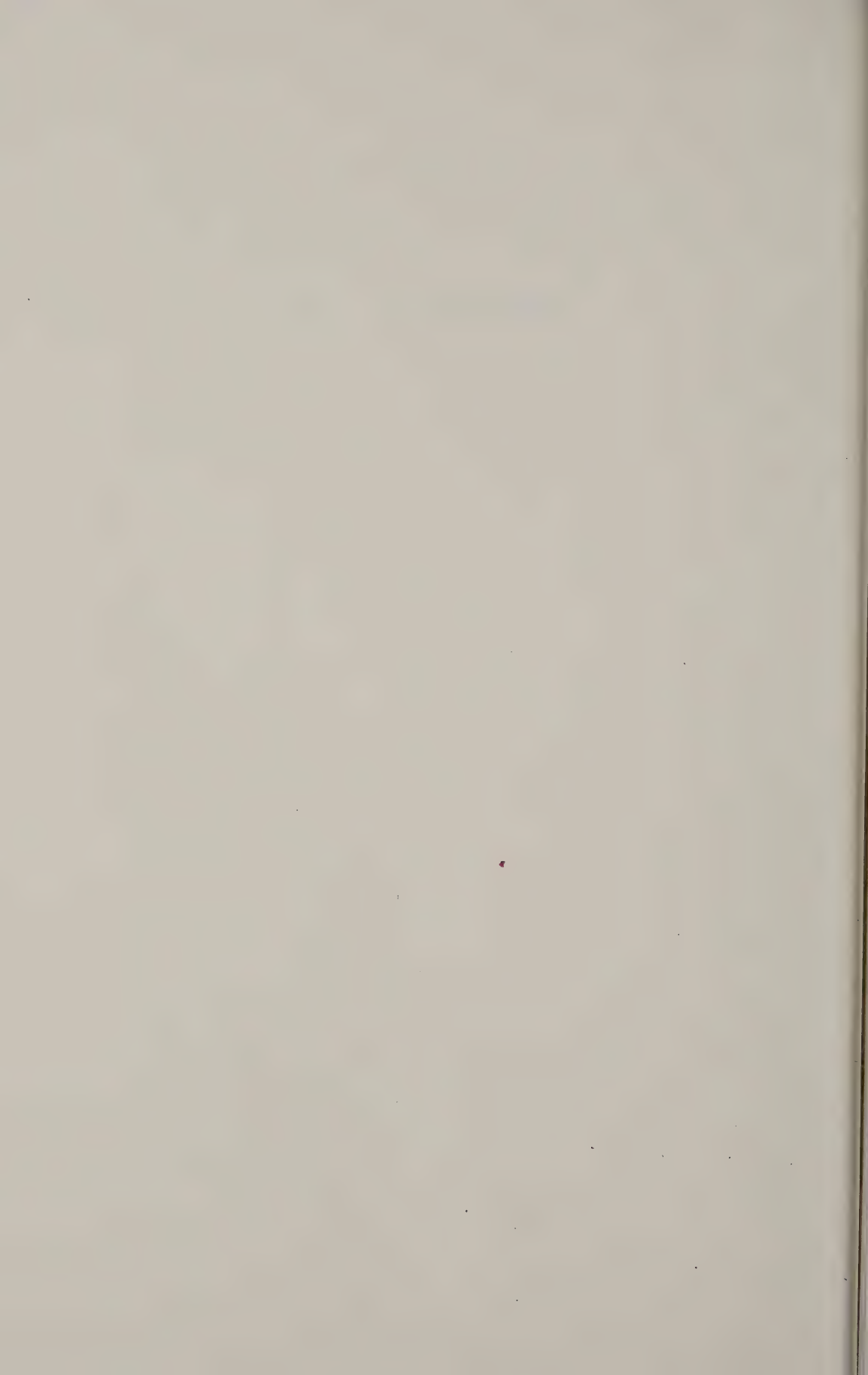
NOTES AND REFERENCES

This biography is an abbreviated reprint of Roger Adams, "Wallace Hume Carothers, 1896-1937," *National Academy of Sciences of the U.S.A., Biographical Memoirs*, 20, 1939.

ROGER ADAMS



Epilogue



THE foregoing biographies present selected aspects of the efforts by which the edifice of chemistry has been built. These efforts, extended over so many years, continue at an increased rate. At certain periods during these years, the edifice appeared to be complete, and there were actually times when it seemed to some chemists that nothing more of any importance could be added, that a solid body of facts and laws were "now" available to be preserved and transmitted in writing and teaching. Yet, new thoughts and facts claimed attention. The feeling grew that each advance was not concluding a tradition but starting an unforeseen development.

Two apparent contradictions accompany this development—the first is the accelerated advance, the second is the attitude toward the future. The greater the body of discoveries was, the more prolific became the production of new ones. Obviously, it is a fallacy to assume that because the field of the unknown was so much greater before, it should have been easier to make new findings. One of the fascinating questions answered in the biographies of these chemists is how they recognized new problems and were successful in finding ways through the unknown. Increasing success established confidence in the future, and here lies the answer to the second of those contradictions. Earlier science relied greatly on the past. As time progressed, the past became enriched and more reliable. The tradition, thus founded, was often invoked against new theories, especially by chemists in their old age who earlier had set the example that the younger chemists now followed. The process almost seemed to conform to a generalization from the law of chemical kinetics which van't Hoff had formulated in 1884, the rate of transformation was proportional to the active mass of the transformable.

In looking back to such changes—their accelerated progress and the men who brought them about—we gain a strong feeling for

the men who brought them about—we gain a strong feeling for the effects of time. The year 1900 seemed so far off to Wöhler in 1843 when he admonished his friend Liebig:

Imagine what will happen in the year 1900 when we shall be returned into carbon dioxide, ammonia and water . . . Who will then be concerned with whether we live in peace or in anger . . .? Nobody, but your good ideas, the new facts you discovered, they will remain known and valued, cleansed of everything that is not permanent, in the most distant times.

It is such a simple truth, and yet it contains the great experience that our lasting work is achieved during the fleeting moment of our present. Thus we see many of these men concentrating on the moment to the point of exhaustion, summoning all their energies like the athlete at the peak of his performance. The effort is dictated by the inner law of the work and the worker, in freedom from a law imposed from the outside. By the height thus reached, we judge the greatness of the man. There is considerable value in the regular duty, faithfully and constantly performed, but we see greatness more in high peaks than in constant levels.

As the effort of the moment extends to the future, so the work on one particular detail has its bearing on the whole of science. When Mitscherlich reported about his investigation of selenic acid to Berzelius, he replied on March 27, 1827: "Thank you for your wonderful discoveries . . . You are going on a straight path to the heart of Nature . . ." To go on this path to the heart of Nature, the chemists require all the meticulous care about methods of operation, recognition and exclusion of impurities, accuracy of measurement, manipulative skill and precise interpretation. Some of the chemists can be occupied completely by these details which they enlarge and refine. Others devote much effort to describing the place of details in a system of chemistry. A third group becomes interested in the industrial applications, while a fourth takes active parts in professional, social, and political affairs. The groups were not sharply separated; in fact, there was a unity between all their special efforts, the unity that Berzelius indicated as leading to "the heart of Nature."

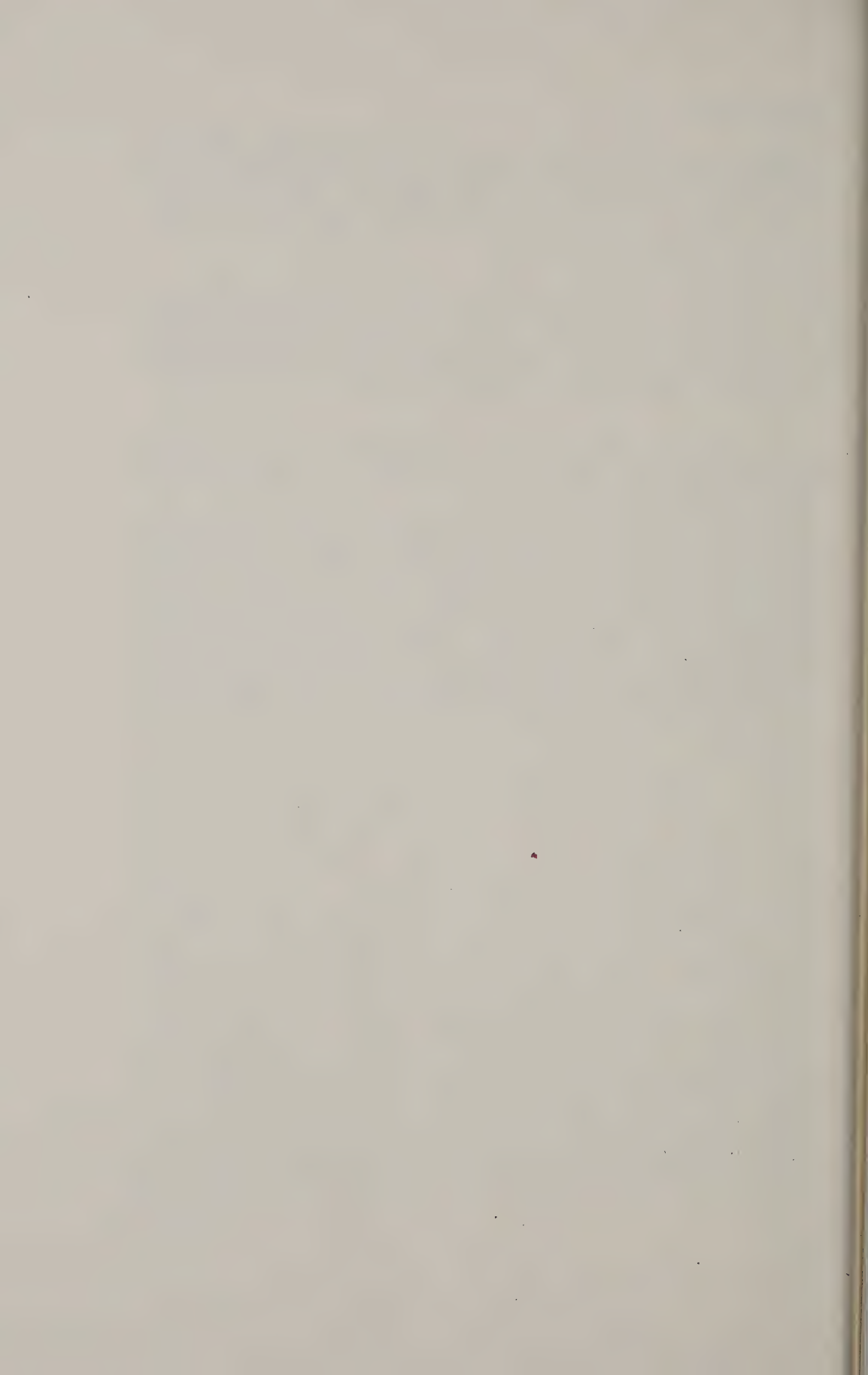
EPILOGUE

When we single out a few men as great, we remain conscious of their own, often expressed conviction that they could not have created their work without that of many others. This recognition is necessary, yet it must not lead to a leveling-off process. In 1792, Lavoisier appealed to his readers:

The theory is therefore not, as I hear it said, the theory of the French chemists, it is mine, and it is a property that I claim before my contemporaries and before posterity. There is no doubt that others have added to it new degrees of perfection . . .

At first glance, this reads like a very egotistic statement, but we must appreciate its wider meaning as a plea to recognize the value of the individual.

Lavoisier experienced, in the most tragic way, the ingratitude of his contemporaries. Fortunately, he was an exception. More often, we find contemporaries who exalted their heroes too highly, a trend that even shows, somewhat, in a few of the older biographies assembled here. Taken together, these biographies enable us to find the right way between ingratitude and hero worship, the way that leads to an understanding and appreciation of our great chemists.



Index

In the following index, those names appearing in *italic type* indicate authorship, while entries in **boldface type** denote biographies.

- Abbaside period, 21
- Abderhalden, Emil, 992
- Abel, Frederick, 630
- absolute zero of temperature, 1200
- absorption of gases, 553
- Abul Hasan Ali bin Sahl bin Rabban, 26
- acetic acid, 680, 706
- acetic anhydride, 1230
- acetone, 127, 290
- acetylene, 1282, 1437
- acetylenic compounds, 1151
- acetylene polymers, 1608
- Achard, Franz Carl, 330, 639
- acid anhydrides, 605
- acid, definition, 1481
- acidum pingue, 269
- aconite, 103
- Acree, S. F., 1142, 1483
- acrolein, 127, 1150
- acrylic acid, 1148
- activity coefficient, 1099
- Adams, Roger, 1599-1611; 1543*
- adenine, 1035
- Adkins, Homer, 1296
- adsorption, 1512
- aeric acid, 256
- aether, 308
- affinities, 321, 491, 681, 1472
- Agassiz, Louis, 813
- Agricola, Georgius, 43
- agricultural chemistry, 376
- Albertus Magnus, 32, 34, 41
- Al-Biruni, 26
- album Graecum, 1584
- albumin, 442
- alchemists, 33
- aldol, 533
- alembic, 24
- Alexanderson, E. F. W., 1516
- Alfred of Sareshal, 32
- alizarin, 740, 765
- alkahest, 85
- alkaloids, 129, 290, 1045
- alkarsine, 576
- Al-Kindi, 21-25**
- alkylation, 1294
- alkyls, 1213
- al-Mamum, 18
- al-Nadim, 16
- alpha-particles, 1353
- Al-Razi, 1; 3; 25-30**
- Altenstein, minister, 484
- Althoff, Friedrich, 1052
- alum, 257, 608
- alumina, 197, 299
- aluminum, 609; chloride, 608
- amalgams, 379
- amber, 1188
- Amberg, Lyle O., 435-451*
- amides, 527
- amino alcohols, 1391
- ammonia, 320, 555; synthesis of, 912, 1305, 1400
- ammonium, 594
- ampho-ion, 1502
- amygdalin, 513
- amyl, 890
- Anaximandros, 9
- Anaximenes, 9
- Anderson, Ernest, 1142
- Andrews, Thomas, 721
- anesthesia, 1260
- angostura bark, 1557

- anil, 628
 aniline, 628
 animal charcoal, 499; fats, 678
Anschütz, Richard, 697-702; 292, 707
Anthony, Richard A., 1185
 anthracene, 740
 anthraquinone, 741
 anthrax, 656
 antidote against arsenic poisoning, 576
 antimony, 55; butter of, 55; sulphide, 330
 antioxidant, 1153
Apolant, H., 1055
Appleyard, Rollo, 479
aqua ardens, 41; — *fortis*, 90, 285; — *regia(is)*, 124; — *vitae*, 101
Aquinas, Thomas, 41
Arabic Chemists, 13-38
 arabinose, 1548
Arago, François, 359-367
 aragonite, 487
Arberry, A. S., 38
 arcanum, 54
 archeus, 58, 102
 Archimedes, 234
Arfwedson, J. A., 392
 argon, 1002
 aricin, 971
Aristotle, 10, 21
Armstrong, Henry Edward, 875-906;
 830, 839, 944, 1154, 1371
Arnaldus Bachuone, called de Villanova, 42
 aromatic arsenicals, 1058; — substances, 130, 701
Arrhenius, Svante, 1093-1109; 954, 1010, 1023
 arsacetin, 1060
 arsenates, 483, 561
 arsenic sulfide, 19, 32
 arsphenamine, 1061
 artificial production of diamonds
 971
 1620
Aschan, Ossian, 1111-1117; 840
Ascoli, A., 1035
Aselli of Cremona, 103
Ashcroft, E. W., 479
Aston, Francis William, 1453-1462
 asymmetry, 648, 952, 1122
 atomic number, 1355; — theory, 338, 670; — volumes, 598; — weights, 525, 823; — weight of nitrogen, 1124; — weight of silver, 1125
 atoxyl, 1060
Auer von Welsbach, Carl, 942
Augustin, Saint, 102
Aula Subterranea, 45
 autoxidation, 1089, 1153
Auwers, Karl von, 1073, 1238
 auxiliary valence, 1240
 auxochrome, 1016
Auzout, Adrian, 160
Avicenna-Ibn Sina, 30-35
Avogadro, Amedeo, 669; — rule, 1207
Azo, R. F., 36
 azotic gas, 246
 azurite, 28
Babcock, Stephen Moulton, 808-813
Babylonian Chemists, 1-12
Bache†, Alfred A., 1551-1562
Bachmann, W. E., 1209-1217
Bacon, Francis, 138
Bacon, Roger, 41
Baekeland, Leo Hendrik, 1181-1190; 770, 1592
Baeyer, Adolf von, 733-747; 634, 1079, 1114, 1371, 1450
 bakelite resins, 1153, 1189
Baker, Herbert Brereton, 1159
Balard, Antoine Jérôme, 659, 885
Ballot, Buys, 952
Bamberger, Ludwig, 1074, 1161
Bancroft, Wilder Dwight, 1245-1261; 770
Banks, Joseph, 467

INDEX

- Barbier, Philippe, 837, 1335
barium, 379
Barral, J. A., 504
Barreswil, Louis Charles Arthur, 964
Barstow, Edwin O., 1228
base—definition, 1481
Basil Valentine, 60
Bates, Frederick J., 1544
Bauer, Hugo, 1055
Baumann, Eugen, 744
Baumé, Antoine, 187
Baxter, Gregory, 824
Bayen, Pierre, 188, 231
Bayer, Friedrich, 635
Beaumont, Élie de, 613
Becher, Johann Joachim, 148, 937
Becke, F., 1566
Beckmann, Ernst Otto, 845
Becquerel, Henri, 1266, 1348
Beddoes, Thomas, 373
Beguín, Jean, 74–79; 61
Béhal, Auguste, 1391
Beilstein, Fedor Fedorovich, 1281
Beilstein, Friedrich Konrad, 290, 728
Bell, J. Carter, 1159
Bell, Ronald Percy, 1469–1488; 1500
Benda, Ludwig, 1060
Benfey, O. Theodor, 703–715
benzaldehyde, 668, 1341
benzedrine, 1395
benzene, 128, 638, 762; — ring, 713
benzil oximes, 1238
benzoates, 816
benzoic acid, 512, 577, 668, 858; sulfimide, 821
benzoin, 628
benzoyl, 512
benzyl alcohol, 668
Bergius, Friedrich, 1286, 1305, 1437
Bergman, Torbern, 234, 255, 608
Bermannus, 43
Bertagnini, Cesare, 666
Bertheim, Albert, 1055, 1060
Berthelot, Marcelin, 675–685; 527, 618, 837, 943, 1292
Berthollet, Claude-Louis, 315–324; 218, 233, 274, 348, 361, 362, 938
beryllium, 1428
Berzelius, Jöns Jacob, 385–402; 288, 319, 349, 354, 379, 483, 509, 611, 940, 1096, 1616
Bestuscheff Nerve Tincture, 300
Beyer, E., 453–463
Bickerton, A. W., 1345
Biermer, Anton, 1048
Bigelow, W. D., 829
Biilman, Einar, 1303, 1495
bile acids, 1447
bilirubin, 1527
biogeochemistry, 1567
biological chemistry, 1107
Biot, Jean Baptiste, 233, 646
Biringuccio, Vannoccio, 43
Bischof, Carl Gustav, 633, 1565
Bishop, Joaquin, 423
Bismarck brown, 1015
Bjerrum, Niels Janniksen, 1489–1506, 1472
Black, Joseph, 211–225; 181, 259, 272
Blackett, Patrick Maynard Stuart, 1358
Blagden, Charles, 273
Blanc, Edmond, 366
Blodgett, Katherine, 1516
Blomstrand, Christian Wilhelm, 868
blowpipe, 391, 422
Boas, Franz, 1134, 1143
Bodenstein, Max, 1208
Boerhave, Herman, 163–176; 87
Bogert, Marsten T., 770, 830, 1317
Bohr, Niels, 1383
Boisbaudran, Lecoq de, 529
Bolito, H., 782
Bolton, Elmer K., 1606

- Boltwood, Bertram Bordon, 1350
 Boltzmann, Ludwig, 1103
Bonhoeffer, Karl-Friedrich, 1299–1311
 Boot, Jesse, 1165
 boraces, 28
 borax, 816
 Bordet, Jules, 1057
 Borelli, Giovanni Alfonso, 170
 Boring, Edwin G., 292
 Borlase, John, 373
 bornyl chloride, 840
 Borodin, Alexander von, 696, 721, 1316
 borohydride, 1426
 boron, 611, 1426
Bosch, Carl, 1397–1408; 943, 1305
 Bouchard, Georges, 357, 450
 Bouchardat, Gustave, 845
 Boudouard, O., 912
 Boullay, P.-F.-G., 444
 Boussingault, Jean Baptiste, 525, 900
 Bouveault, Louis, 844, 1335
Boyle, Robert, 135–148; 61, 84, 133, 937
 Bragg, W. H., 1567
 Bragg, W. L., 1567
 Brande, William Thomas, 468
 brass, 197
 Brauer, Eberhard, 1026
 brazilin, 438
 Brecht, Julius, 844, 1115
 Bretschneider, H., 1558
 Brickwedde, Ferdinand Graft, 1459
 Bridgman, P. W., 825
 Brieger, Walter, 133
 Brill, Rudolf, 1401
Briner, E., 1119–1127
 Brøgger, W. C., 1565
 bromine, 1224
 Brongniart, Alexandre, 510
Brønsted, Johannes Nicolaus, 1469–1488; 1080, 1491
Brougham, Henry, 211–225
- Browne, Charles A., 829
 brucine, 129
 Brühl, J. W., 1114
 Brugnatelli, 511
 Brunck, Heinrich von, 943
 Buchern, Urban Gottfried, 938
 Bucholz, Christian Friedrich, 487
 Buff, Heinrich, 515
 Buffon, George Louis Leclerc de, 365
Bugge, Günther, 293–302
 Bundy, F. P., 979
Bunsen, Robert Wilhelm, 573–581; 941
 Bunte, Hans, 1302
 Burg, A. B., 1429
 Burton, William M., 176
 butadiene, 1284
 butane, 531
 Butler, Nicholas Murray, 770
Butlerov, Alexander Mikhailovich, 687–696; 741
 Butterfield, Lyman H., 314
 butyl alcohol, 706
 butylene, 396
 butyric acid, 439
 Byron, Lord, 950
- Cacodyl, 576, 891, 1213**
 Cadet's liquid, 576
 cadinine, 842
 cadmia, 197
 caesium, 579
 Cagniard-Latour, Charles, 650
 Cahours, Auguste André Thomas, 527
 Caillot, Amedée, 837
 calamine, 197
 calcareous salt of sorrel, 258
 calcite, 487
 calcium, 379; — hyperchlorite, 1227
 calculus, 101
 Callendar, H. L., 1348
 caloric, 175; — machine, 1208

INDEX

- calorimeter, 825
- Calvin, Melvin, 1544
- calx of mercury, 270
- Cambeceres, Jules de, 441
- Campbell, Murray, 1232
- camphene, 836, 837
- camphor, 19, 24, 198, 1115, 1163, 1167
- candles, 441
- Candolle, A. P. de, 497
- cane sugar, 330, 678
- Cannizzaro, Stanislao, 661-674;**
288, 901
- Cap, P. A., 188
- capacity for heat, 592
- capillarity, 752
- carbohydrates, 1537
- carbon disulfide, 859
- Carbonelli, Giovanni, 42
- carbonium compounds, 745
- carbon monoxide, 1438
- carbon tetrachloride, 888, 1230
- Carius, Ludwig, 721
- Carlisle, Anthony, 377
- Carlson, Oscar, 869
- Carnot, Sadi, 791
- Caro, Heinrich, 769, 942, 987, 1292
- Caron, Henri Louis Maurice, 612
- carone, 1282
- carophyllene, 842
- Carothers, Wallace Hume, 1599-1611**
- Carra de Vaux, 38
- Carriere, J., 402
- Cassella, Leopold, 635
- Cassius, Andreas, 132
- catalysis, 514, 1478, 1498
- catalyst, definition, 397
- catalytic dehydrogenation, 1284
- Cavendish, Charles, 229, 1001
- Cavendish, Henry, 227-238, 217**
- Caventou, Jean Baptiste, 444
- cedrilet, 636
- celestine, 484
- cellular tissue, 442
- cellulose, 871; — acetate, 1198
- ceration, 29
- cerebroside, 1321
- cerium, 289, 299
- cesium, 1514
- cetyl alcohol, 441, 526
- Chadwick, James, 1343-1363;*
1358
- chalcophile, 1568
- chalk, 181
- Challenger, Frederick, 1157-1179*
- Chancourtois, de, 724
- Chaptal, Jean Antoine Claude, 348, 938
- Chardonnet, Count de, 1197
- Charleton, Walter, 88
- Chase, Fred L., 1591
- Le Chatelier, Henry, 907-920**
- cheese, 810
- chemical dynamics, 1023; — equilibrium, 911; — homology, 1017; — structure, 711
- chemistry without substances, 1024
- chemotherapy, 1043
- Chevreur, Michel-Eugène, 435-451;**
680, 969
- Chichibabin, 1213
- Child, C. D., 1523
- Chittenden, Russel H., 770, 817
- chloral, 532, 544
- chlorine, 247, 319, 351, 379, 530
- chlorium, 351
- chloroform, 544, 1230
- chloromethane, 735
- chlorophyll, 289, 1088, 1369, 1530
- chloroprene, 1608
- Choay, E., 1396
- cholanic acid, 1449
- cholesterin, 441, 1447
- cholic acids, 461, 1327
- chromatography, 1371
- chrome tanning, 1197
- chromic compounds, 1493; — oxide, 401, 510

- chromium, 964
 chromophore, 1016
 chrysoidine, 1016
 Chugaev, L. A., 730
 Church, Arthur H., 760
 chyle, 103
Ciamician, Giacomo, 1085-1092;
 291
 cinchonine, 444
 cinnabar, 329
 citrene, 836
 citric acid, 258
 Claisen, Paul, 1161
 Clark, Jonas Gilman, 1133
 Clarke, Frank W., 807
 Claude, George, 1006
 Clausius, Rudolf, 1099
 Clement, Nicolas, 364
 Cleve, Per T., 1101
 Cliffe, W. H., 945
 Cloez, François Stanislaus, 667
 cloud seeding, 1518
 Clowes, Frank, 1164
 coagulation, 29
 coal research, 1436; — tar, 627,
 761, 858
 cocaine, 1368
Cohen, Ernst, 947-958; 1256
 Cohnheim, Julius, 1042
 Coleridge, Samuel Taylor, 375
 Collie, John Norman, 1079
 colloidal substances, 564, 1255,
 1308
 color blindness, 338; — harmony,
 1029
 combining weights, 323, 327
 combustion chemistry, 1302
 Comenius, J. A., 138
 complex acids, 827
 composition of water, 273
 Compton, Piers, 659
 Comte, Auguste, 949
 Conant, James B., 826
 condensation, 1089
 conhydrine, 637
 coniine, 637
 conjugation, 1443
 contact catalysis, 1259
 contagium vivium, 654
 Cook, G. H. H., 1345
 Cooke, Josiah Persons, 411, 822,
 1248
 Cooper, Edward, 924
 coordination theory, 1239
 Copernicus, 49
 copper, 90; — sulfate, 816; —
 vitriol, 90
 Corner, George W., 314
 corpuscular philosophy, 140, 207
 Correns, C. W., 1584
 corresponding states, 753
 corrosive sublimate, 356
 cosmic material, 1107
 coulometer, 476
 Coulomb, Charles Augustin, 234
Couper, Archibald Scott, 703-715;
 288
 Courtois, Bernard, 364
Courtot, Charles, 1333-1342
 covalent, 1081
 cracking, 1287
Crell, D. Lorenz, 253-261
 croconic acid, 461
 Crombie, A. C., 31
 Crookes, William, 630, 769, 1349
 Cross, Charles Frederick, 1197
 crucible steel, 470
 crystallography, 483, 1569
 cucurbit, 24
 Cullen, William, 213
 cumidine, 631
 Curaudau, François René, 508
Curie, Marie, 1263-1275; 1348
 Curie, Pierre, 1267
 Curtis, John G., 1317
Curtius, Theodor, 573-581
 Cutbush, James, 314
Cuvier, Georges, 227-238
 cyanic acid, 396, 511, 637
 cyanogen, 365, 511, 594, 1213

INDEX

- cyclization, 1286
- cyclooctatetraene, 291, 1369
- cymene, 837
- D'Alambert, 245
- Dale, Julian K., 1543
- Dalton, John, 333-342;** 246, 382, 394, 669
- Dana, James Dwight, 415, 820
- Dann, George Edmund, 302
- D'Ans, J., 945
- Darcet, Jean, 188
- Darmstaedter, Ernst, 45
- Daubrée, Auguste, 492
- Davis, Tenney L., 210
- Davy, Humphry, 369-384;** 319, 339, 349, 394, 938
- Debierne, André, 1348
- Debray, Henri Jules, 613, 968
- Debye, Peter, 1501
- deflagrator, 414
- deflocculation, 1260
- Delafosse, Gabriel, 646
- Delhoume, Léon, 366
- d'Elhujar, Fausto and Juan José, 257
- De Lithiasi, 100
- Democritos of Abdera, 10
- Denainvilliers, de, 182
- density of the earth, 235
- deoxyribonucleic acids, 1035
- Deparcieux, Antoine, 267
- depsides, 992
- Descartes, Rene, 140
- Desormes, Charles-Bernard, 364
- deutoxide of barium, 353
- Deville, Charles Sainte-Claire, 619
- Déville, Henri Sainte-Claire, 601-623;** 510, 909, 962
- Dewar, James, 753, 1004
- Dezeimeris, John, 88
- dialysis, 564
- diamagnetic, 478
- diamidoazobenzene, 1015
- di-amino-triphenyl methane, 1078
- diazomethane, 1140
- di-bromo-succinic acid, 766
- dichlorodifluoromethane, 1591
- Dieffenbach, Johann, 589
- Diels, Otto, 1450
- dielectric constant, 1098
- Diergart, Paul, 301
- diffusion of gases, 557; — of liquids, 557
- Digby, Kenelm, 147
- digestion, 460
- dihydrocarvone, 1090
- Dilthey, Walther, 1175
- dilution law, 1023
- dimorphism, 487
- dinitrobenzene, 760
- dinitronaphthalene, 760
- dinitro-triphenyl methan, 1078
- diphenylguanidine, 631
- Dippel, Johann Konrad, 187
- Diqaru (a pot), 3
- disintegration theory, 1465
- dissociation, 616, 1103
- Döbereiner, Johann Wolfgang, 724
- Dellond, George, 474
- dolomite, 484
- dolphin, 439
- Dorn, Max, 1349
- double atoms, 396
- Dove, Heinrich, 739
- Dow, Herbert Henry, 1219-1232;** 943
- dragon's blood, 604
- Drechsel, E., 1317
- Drescher-Kaden, F. K., 1578
- Drolenvaux, Abraham, 167
- Drummond, Thomas, 423
- dualism, 397, 527, 884
- dualistic ideas, 398
- Dubais—Muhammed ibn Yazid, 23
- Dubois, René J., 659
- Duchesne, Joseph, 78
- Duclaux, Emile, 658
- Duecker, W. W., 932
- duelech, 100
- Dufraisse, Charles, 1145-1156*

- Duhamel du Monceau, Henri-Louis, 177-183**
 Duisberg, Carl, 943
 Dulong, Pierre Louis, 391, 401, 488, 592
Dumas, Jean Baptiste, 521-533; 290, 398, 446, 606, 620, 962
 Duppa, B. F., 771
 Du Pont, Pierre Samuel, 271
 Dupuytren, Guillaume, 357
 Dutrochet, Rene Joaquin, Henri, 567
 Dutronne de la Couture, Jacques Francois, 330
Duveen, Denis I., 263-281
 Duverney, Joseph-Guichard, 160
 Dyar, H. G., 777
 dyestuffs, 320, 635, 757, 1016, 1048

 Eastman, George, 1186
Edelstein, Sidney M., 757-772
 Edgeworth, Maria, 375
 Edison, Thomas, 1268
 Edlund, E., 1097
 Egloff, Gustav E., 1295
Ehrlich, Paul, 1039-1063; 942, 1107
 Einhorn, Alfred, 1368
Einstein, Albert, 1203-1208; 1029, 1291
 Ekeberg, Anders Gustaf, 389
 Ekstrand, A. G., 1101
 electrical conductivity, 1098
 electric eel, 236
 electric furnace, 965, 975
 electricity through gases, 1347
 electrochemistry, 628, 1027, 1255, 1304
 electrolysis, 578, 1123, 1205, 1227, 1474, 1496
 electromagnetic induction, 475
 electronic theory of valency, 1383
 emanation, 1009
 Emich, Friedrich, 1327
 Empedocles, 10
 endothermic reactions, 683
 energy relationships, 1025
 Engler, Karl, 1235, 1302
 entropy, 792, 1206
 enzymes, 992, 1089
 Epicuros, 11
 Epilogue, 1613-1617
 equation of state, 753
 equilibrium, 679, 793
 equivalents, 399
 Ercker, Lazarus, 43, 45
 esters, 595, 681
 ethane, 531
 ethereal oils, 836
 ethyl acetoacetate, 1069
 ethylene, 396, 1284
Étienne, René, 773-782
 ethanol, 711
 Euclid, 21
 eudiometer, 233
 Euler, Hans von, 1109
 Evans, Ward G., 1297
 Evans, William Lloyd, 1136
Eve, A. S., 1343-1363
 exothermic reactions, 683
 explosives, 684

Fabre, René, 1085-1092
 Fahlberg, Constantin, 821
 Fahrenheit, Gabriel Daniel, 219
 Fairchild, David, 1189
 Fajans, Kasimir, 824
Faraday, Michael, 465-480; 286, 380, 431, 570, 705, 767, 1268, 1361
Farber, Eduard, 7-12, 39-46, 283-292, 315-324, 325-332, 675-685, 935-945, 1019-1030, 1365-1374, 1441-1451, 1613-1617
 Favorsky, Alexej E., 1282
 Fechner, Gustav Theodor, 1028
Felix, Kurt, 1031-1037
 fenchone, 849
 Ferme — Général, 266

INDEX

- fermentation, 199, 649, 741, 1141
- Fernel, Jean, 57
- ferric bromide, 1225
- fertilizer, 546
- fibrin, 442
- fifth element, 54
- Figuiier, Pierre Oscar, 499
- Fihrist, 16
- Findlay, Alexander*, 1245-1261
- Fischer, Emil, 981-995**; 289, 633, 736, 860, 1073 1423, 1435
- Fischer, Franz, 1433-1440**
- Fischer, Hans, 1525-1533**
- Fischer, Otto, 633, 984
- Fisher, George P., 417
- Fittig, Rudolf, 819
- flame reactions, 579; — tests, 145; — temperatures, 1304
- fixed air, 230, 243
- Flexner, Simon, 1315
- flocculation, 1260
- Flourens, Pierre Jean Marie*, 343-357
- Flürschheim, Bernard, 1213
- fluor acid, 247
- fluorine, 965
- fluo-silicic acid, 258
- Fontenelle, Bernard Le Bouvier de*, 149-161; 446
- Forbes, G. S., 824
- formaldehyde, 741, 816
- formic acid, 527
- Fourcroy, Antoine François de, 188, 274, 346, 940
- Fourneau, Ernest*, 1389-1396
- Franck, James, 1308
- Frankenburger, Walter, 1401
- Frankland, Percy, 660, 889, 1336
- Franklin, Benjamin, 208, 309, 785
- Frasch, Herman, 921-933**
- free radicals, 1309
- Fremy, Edmond, 965
- French, John C., 829
- Frerichs, Friedrich von, 1047
- Fresenius, Carl Remigius, 629
- Fresnel, Agustin, 777
- Freudenberg, Karl, 1429
- Friedel, Charles, 529, 1121
- Fritsche, Carl Julius von, 628
- Froben, Johannes, 50
- Fuchs, Johann Nepomuk, 485
- fuchsin, 632
- fulminate of mercury, 1138
- fulminic acid, 396, 511, 549, 1138, 1441
- Fulton, John F., 148, 417
- Furni Novi Philosophici, 120
- Gadolin, Johann, 299, 1116
- Gahn, Johan Gottlieb, 390
- Galen, 31
- Galileo Galilei, 137
- gallium, 724
- Garbers, Karl, 23
- garlic, 1373
- gas, van Helmont's definition, 92; — aetereum ac vitale, 96; — flammeum, 94; — fulmiguosum sive endemicum, 94; — pingue, 94; — siccum, 94; — sulphureum, 94; — sylvestre, 93; — uvae, 94; — ventosum, 94; — vini, 94
- gas-mask, 1199
- gasoline, 1287
- gasometric methods, 579
- Gassendi, Pierre, 140
- gastric juice, 102
- Gautier, Armand, 969, 1006
- Gay-Lussac, Joseph-Louis, 359-367**; 233, 247, 319, 400, 541, 938, 1100
- Geber, 16
- Geiger, Hermann, 1350
- geochemistry, 1565
- Geoffroy, Claude-Joseph (Geoffroy the Younger), 440, 608
- Geoffroy the Elder, 321
- geometric atomism, 159

- Gerhardt, Carl Charles Friedrich, 526, 691, 710, 880, 881, 1047
 germanium, 724, 1576
 Getman, Frederick H., 829
 Geuther, 894
 Gibbs, F. W., 176
 Gibbs, George, 410
Gibbs, Josiah Willard, 783-803; 291, 751, 912, 1023, 1250
 Gibbs, Wolcott, 430
 Gilbert, Davies, 373
 Girard, Charles, 632
 Glaser, Christophe, 151, 275
 glass, 307
 Glatfeld, J. W. E., 1137
Glauber, Rudolph, 115-134; 938
 glucose, 814, 1537
 glycerine, 257, 440
 glycols, 531
 glycoll, 766
 Gmelin, Christian Gottlob, 455;
 Johann Friedrich, 457
Gmelin, Leopold, 453-463; 391, 508, 938, 1447; - Paul, 1402
 Goethe, Johann Wolfgang, 392, 939
 gold, 33, 90; — in sea water, 1307
 Gold Drops of General de la Motte, 300
 Goldschmidt, Hans, 1427
 Goldschmidt, Richard M., 1372
Goldschmidt, Victor Moritz, 1563-1586
Gomberg, Moses, 1209-1217; 1282, 1445
 Gomes, B. A., 444
 goniometer, 488, 489
 Gortner, R. A., 570
 Gough, John, 336
 Graebe, Carl, 740, 1016
Graham, Thomas, 551-571; 469
 grape sugar, 331
 Gray, Whitlaw, 1009
 Griess, Peter, 630, 941
 Griffin, Roger, 1196
Grignard, Victor, 1333-1342; —
 reagent, 1170
 Grimm, Melchior, 189
 Griswold, Thomas, 1222
 Groth, Paul von, 985, 1372, 1566
 Grove battery, 517
 Guerlac, Henry, 225
 Guettard, Jean Etienne, 265
Guggenheim, Edward Armand, 1489-1506; 1483
 Guldberg, Cato Maximilian, 681, 796
 Gunning, J. W., 953
 gunpowder, 309
Guye, Philippe-Auguste, 1119-1127
 Guyon, Félix, 655
 gypsum, 197
Haber, Fritz, 1299-1311; 535-549; 912, 1370
 Hadfield, Robert, 471
 Hale, William J., 1230
 Hales, Stephen, 174, 243
 Hall, G. Stanley, 1133
 Hall, Lyman B., 822
Hall, Marie Boas, 135-148
 halochromism, 1214
 Hamilton, William, 708
 Hammett, Louis Plack, 1082
 Hann, Ray M., 1549
Hantzsch, Arthur Rudolf, 1065-1083; 857, 1238
 haptophoric group, 1053
 Harcourt, Vernon, 1377
Hare, Robert, 419-433; 312, 407
 harmaline, 1558
 Harned, Herbert S., 827, 1109
 Harper, William Rainey, 1134
 Harries, Carl, 990
 Harrison, W. E., 926
 Harrow, Benjamin, 829
 Hart, E. B., 811
Hartley, Harold, 875-906; 829
 Hartmann, R. Julius, 62
 Harun al-Rashid, 18

- Harvey, William, 651
Hastings, Charles S., 789
Hata, Sahashiro, 1055
Hattorn, Harrison, 1232
Haüy, René Juste, 391, 486
Hautefeuille, Jean de, 618
Haynes, Williams, 921–933; 1181–1190; 1191–1201; 1219–1232; 1409–1420; 1587–1597
heavy hydrogen, 1460
Hedenburg, Oscar, 1137
Heidenhain, Rudolf, 1042
Hein, Franz, 1083
Helperich, Burckhardt, 981–995
helium, 754, 1003, 1271
Hellot, Jean, 938
Helmont, Joan Baptista van, 81–114;
 141, 147
hematine, 1088
hematite, 28
hematology, 1051
hematoxylin, 438
Hemet, Christopher, 118
hemin, 1529
hemlock, 637
hemoglobin, 1155
Hempel, W., 1068
Henle, Jacob, 655
Henrich, Ferdinand, 1142
Henry, Joseph, 414, 429, 478, 785
Henry, William, 239–251; 412, 808
Hepp, Eduard, 742
Heracleitos, 9
Herschel, John, 474; William, 298, 1081
Herter, Christian A., 817
Herty, Charles H., 770, 820, 1547
Hesiod, 9
Hess, Germain Henri, 392
Heumann, Karl, 744
Hevesy, George de, 1485
Hewitt, Abraham, 924
hexachlorobenzene, 473
hexaphenylethane, 1212
hexosamine, 1322
Higgins, William, 338, 715
high pressure apparatus, 1402
Hildebrand, Bengt, 260; — Joel H., 827
Hillpern, Edmund P., 1029
Hindu calendar, 236
Hippocrates, 21
Hirst, Edmund Langley, 1549
Hisinger, Wilhelm von, 388, 439
histones, 1035
Hittorf, Wilhelm, 1105
Hitzig, J. E., 738
Hjelt, Edvard, 1115
Hlasiwetz, Heinrich Hermann, 1559
Hoard, William D., 809
Hofer, Ferdinand, 187, 208
Hönigschmidt, Otto, 824
van't Hoff, Jacobus Henricus, 947–958; 289, 711, 1010, 1103, 1122
Hoffmann, Friedrich, 170, 187, 639
Hofmann, August Wilhelm von, 625–640; 505–520; 301, 442, 531, 555, 740, 762, 834, 986
Holdermann, Karl Friedrich, 1397–1408
Hollandus, Isaac, 90
Holleman, Arnold Frederik, 958
Holmberg, Bror, 874
Holmes, Harry N., 820
Holmyard, E. J., 36
Holtz, Julius, 636
Homberg, Guillaume, 148
homology, 524
honeystone, 299
Hooke, Robert, 139
Hooker, Elon H., 1187
Hopkins, A. W., 828
Hoppe-Seyler, Felix, 1033
Hopwood, Arthur, 333–342
hordein, 332
Hudson, Claude Silbert, 1535–1550
Hübner, Hans, 808, 859
Hückel, Walter, 1111–1117
Huisgen, Rolf, 1451
Hulett, G. A., 1544

- Humboldt, Alexander von, 233, 361, 541
 Humphrey, George, 811
 Husain, M. Hidayat, 36
 Huygens, Christian, 142
 hydrate of chlorine, 471
 hydrazine, 1445
 hydrindamine, 1169
 hydrochloric acid, 72, 319
 hydrocyanic acid, 513
 hydrogen, 146, 232, 379, 1270;
 — ion concentration, 1479; sulfide, 321
 hydrogenation, 1286
 hydrometer, 267
 hydroquinone, 576, 1068
 hydroxides of aluminum, 1371
 hydroxylamine, 857
 hyle, 10
 Hypsicles, 21

 Ibn Abi Usaibia, 27
 Ibn Khallikan, 25
 Ibn Sina — see Avicenna
 Icy Noctiluca, 143
 Ihde, Aaron J., 385–402, 465–480, 805–830
 illuminating gas, 869
 indigo, 320, 437, 628, 740, 984
 indole, 740
 indoxyl, 744
 inert gases, 1501
 inflammable air, 230
 influence of light, 1089
 inorganic chemistry, 1237, 1285
 iodine, 289, 354, 490; — pentafluoride, 970
 iodoform, 1088
 iodonium compounds, 1168
 ion, 286
 ionic equilibrium, 1475; — substitution in minerals, 1570
Ipatieff, Vladimir N., 1277–1298
 Irvine, James C., 705
 Isbell, Horace S., 1545
 isocyanic esters, 530
 isomerization, 842, 1257
 isomers, 397
 isomorphism, 720
 isonitriles, 637
 isoprene, 845, 1282
 isosterism, 1607
 isotonic coefficient, 1104
 isotope, 1357, 1485
 isotopic analysis, 1458

Jabir Ibn Hayyan, 16–21
 Jacobi, Leonhard, 1185
 Jacobs, Walter A., 1322
 Jackson, C. Loring, 1134
 Jaenecke, Ernst, 1401
 Jafer al-Sadiq, 17
 Jagnaux, R., 187
 Japp, F. R., 702
 Jastrow, Joseph, 446
 Jenner, Edward, 656
 Jensen, Aksel Tovborg, 1504
 Jerrold, W., 479
 Jørgensen, S. M., 1242, 1485
 John of Rupescissa, 53
 Johnson, Samuel, 166
 Joliot-Curie, Irène, 1268
 Jones, Francis, 1159; — H. Bence, 479; — Lauder W., 1142

 Kahlenberg, Louis, 812
 Kahn, Robert, 1055
 Kaiser-Wilhelm-Institut, 993
 kali plant (glasswort), 181
 Kalle, W., 635
 Kamerling Onnes, Heike, 749–755
 Kappeler, Carl, 856
 Karrer, Paul, 1062, 1242
 Kastner, Karl Wilhelm Gottlieb, 540
 Kehrmann, Fritz, 1214
Kekulé August, 697–702; 288, 292, 736, 896, 951, 1139
 Kendall, James, 714
 Kennedy, Norman F., 1547
 Kerker, Milton, 163–176

INDEX

- kerosene, 722
 keto esters, 1069, 1137
 Keyes, F. Donald, 1201
 Kharash, M. S., 1342
 khellin, 1559
 Kihlmeyer, F. X., 455
 kinetics, 1478
Kingdon, Kenneth H., 1507–1523
Kipping, Frederic Stanley, 1157–1179
 Kirchhoff, Gustav Robert, 578
 Kitab al Shifa, 31
 Kjedahl, Johann, 500
Klaproth, Martin Heinrich, 293–302; 329, 388, 389, 456, 484
Klason, Johan Peter, 865–874
 Klaus, Karl Karlovich, 689
 Klickstein, H. S., 280
 Klooster, H. S. van, 944
 Knorr, Ludwig, 987, 1301
Koch, Herbert, 1433–1440
Koch, Richard, 641–660; 1039, 1063
 Koch, Robert, 643, 1052
 Köhncke, O., 199
 Koenigs, Wilhelm, 292
 Kohlrausch, Friedrich, 1097, 1105
 Kolbe, Hermann, 680, 888, 903
Kopp, Hermann, 583–599; 518, 900
 Kopp, Johann Heinrich, 586
Kossel, Albrecht, 1031–1037
Kraus, Charles A., 783–803
 Kraus, Paul, 16
 Krehl, Ludwig, 1034
 Kremers, Edward, 812
 Kruif, Paul de, 828
 krypton, 1005
 Kühne, Willy, 862
 Kuenen, Fritz, 754
 Kuffner, Franz, 1558
 Kuhlmann, Charles-Frédéric, 940, 1327
 Kuhn, Richard, 1374
 Kunckel, Johann von Löwenstern, 118, 144, 195, 255, 639
 Kundt, August, 985
 Kunheim, Hugo, 636
 Kuznetsov, B. G., 210, 731
 Kvalheim, Aslak, 1578
 La Caille, Nicolas Louis de, 265
 lactic acid, 257, 894, 897
 La Forge, F. B., 1543
 Laire, George de, 632
 L'Allemand, C., 458
 Lamb, Arthur B., 1548
 Lambert, Johann Heinrich, 1029
 La Mer, Victor K., 1475
 Landolt, Hans, 1423
Langmuir, Irving, 1507–1523; 1593, 1603
 Laplace, Pierre Simon de, 232, 272
 Lapworth, Arthur, 1163
 latex, 190
 Laue, Max von, 1567
 Laurent, Auguste, 398, 880, 881
 Lauth, Charles, 764
Lavoisier, Antoine Laurent, 263–281; 175, 231, 288, 371, 608, 971, 1617
 Lawrence, Ernest O., 1271
 lead, 34; — acetate, 11
 Lebeau, Paul, 979
 Le Bel, Joseph Achille, 529, 711, 951, 1122
 Leblanc, Nicolas, 776, 940
Le Chatelier, Henry, 907–920
Leicester, Henry M., 201–210, 687–696, 717–732
 Leiden bottle, 236
Lemay, Pierre, 601–623; 192, 324, 451
 Lember, Max E., 824
Lemery, Nicolas, 149–161; 188, 191, 275, 288
 lemon juice, 258
 Le Mort, James, 167
 Lender, Joe, 1319
 Lenz, Heinrich, 1097

- Leonhardi, Johann Gottfried, 297, 939
 Leonceno, Niccolo, 49
Lepsius, Bernhard, 625-640
 Leroy, Jean Baptiste, 267
 leucite, 299
Levene, Phoebus Aaron Theodor, 1313-1324; 1035
 Leverkusen, Carl, 943
Levey, Martin, 1-6, 13-38
 Lewis, Gilbert N., 825, 1382, 1475, 1497
 Lewis, W. Lee, 1142
Libavius, Andreas, 65-73
 lichen of Iceland, 332
Lieb, Hans, 1325-1331
 Liebermann, Karl, 740, 1016
Liebig, Justus von, 535-549; 738, 880, 938, 940, 1025, 1446, 1616
 Lifschitz, Israel Z., 1241
 lignin, 871, 1437
 Lilienfeld, Leon, 1035
 limestone, 779
 limonene, 841
 Lindemann (Lord Cherwell), 1457
 Linnaeus, Karl, 1106
Lippmann, Edmund O. von, 193-199; 36, 498
 liquefaction, 477
 liquid chlorine, 472
 List, Adolph, 821
 Lister, Joseph, 644
 lithium, 1223
 lithophile, 1568
Little, Arthur Dehon, 1191-1201
 lobeline, 1448
 Lockemann, Georg, 581
 Lockyer, Norman, 1003
Lomonosov, Mikhail Vasil'evich, 201-210
 London, E. S., 1321
 Long, John H., 817
 Lowitz, Tobias, 331
 Lowry, Thomas, 1167
 1632
 Lubbock, John, 879
 luminous stones, 197
 luna cornea, 145
 Lunge, Georg, 943
 McCay, L. W., 1539
 McCollum, Elmer V., 811
 McKie, Douglas, 105
 McPherson, William, 830, 1142
 Macdonald, William, 1350
 Mach, Ernst, 1027
 Maclean, John, 406
 Macneven, William J., 428
 Macquer, Peter Joseph, 297, 608, 939
 Magendie, François, 444
 magenta, 764
 Magie, William F., 1539, 1549
 magisterium, 71
 magistrery of bismuth, 152
 magnesia, 197, 214
 magnesia alba, 285; — nigra, 256; — usta, 285
 magnesium, 379, 1230
 magnetic rotation, 767
 Magnus, Gustav, 392, 963
 Maisch, John M., 925
 malate of lead, 511
 Mansfield, Charles Blackford, 630
 Manardi, Giovanni, 49
 margaric acid, 438
Marggraf, Andreas Sigismund, 193-199; 295, 330
 Marignac, Jean Charles, 823
 marine ether, 188; — salt, 187
 Markovnikov, Vladimir Vasil'evich, 692, 1114
 Mary the Jewess, 3, 11
Marotta, Domenico, 661-674
Marquand, Carl B., 1277-1298; — *Helen H.*, 1277-1298
 Marquardt, Martha, 1055
 Marsden, E., 972
 Martius, Karl Alexander, 630, 634, 635, 769

INDEX

- Mason, H. S., 714
 mass spectrograph, 1458
 Matignon, Camille Arthème, 251
 Matteucci, Carlo, 478
 Matthews, J. M., 770
 mauve (dyestuff), 632, 760
 Maxwell, James Clerk, 291, 705, 790
 Maya astronomy, 1411
 Mayow, John, 147
 meat extract, 549
 ter Meer, Edmund, 742
 Meldola, Raphael, 771
 mellitic acid, 299
 Melloni, Macedonio, 664
Mendeleev, Dmitri Ivanovich, 717-732; 290, 591, 695, 1242, 1280
 Mendelssohn-Bartholdy, Paul, 635
 Menshutkin, Boris N., 209, 724, 1280
 menstrum, 172
 menthol, 845
 menthone, 1090
 Merck, Georg, 630
 mercury, 19, 33, 97, 159, 173;
 — sickness, 1428
 Merian, J. B., 926
 Merz, August, 770
 Merz, Victor, 1235
 Mesmer, Friedrich Anton, 274
 mesoxalic acid, 857
 metal-ammonia salts, 1241
 metallo-organic compounds, 1593
 metallurgy, 913
 metaphosphoric acid, 562
 Metherie, Julien Offroy de la, 398
 methyl alcohol, 526, 680
 methyl chloride, 735
 methylene blue, 1049, 1446
 methylene dissociation, 1139
 methylheptenone, 1336
 Metzger, Helene, 176, 446
 Meyer, Ernst von, 1070
 Meyer, Kurt Hans, 1079
 Meyer, Lothar, 723
 Meyer, Richard, 853-863
Meyer, Victor, 853-863; 580, 823, 849, 1073, 1114, 1212
 Michael, Arthur, 1131
 Michaelis, Leonor, 1043, 1502
 Michell, John, 234
 Michelson, Albert A., 1134, 1143
 micro-analysis, 1327
Midgley, Thomas Jr., 1587-1597
 Miers, Henry, 1002
 Miescher, Friedrich, 1034
 Miles, Wyndham D., 303-314; 403-417; 419-433
 milk sugar, 257, 1539
 Milkwort (*Polygala amara*), 182
 Mill, John Stuart, 672
 Miller, Samuel, 313
 Milly, Adolphe de, 442
 mineral analysis, 607; — oils, 614;
 — waters, 145
 Mitchell, Thomas Duché, 313
 Mitchill, Samuel Latham, 374
Mitscherlich, Eilhardt, 481-493; 391, 461, 473, 560, 633, 735, 834, 1616
 Mittasch, Alwin, 1305
Moissan, Henri, 959-979; 942, 1337, 1424
 molecular refraction, 1123; — transposition, 1394
 molybdaena nitens, 257
 Mond, Ludwig, 779, 943
 Monge, Count Gaspard, 232, 273
 Monnet, Grimoald, 265
 monoamino acids, 1036
 Montesquieu, 213
 Moore, Tom Sidney, 1083
 Morgan, John, 305, 926; — G. T., 1242
 Morgenroth, Julius, 1055
 Morhof, 99
 morphine, 129, 444, 515
 Morse, Harmon N., 820
 Morveau, Louis Bernard Guyton de, 217, 274

- Mosander, Carl Gustav, 392
 Moseley, Henry Gwyn Jeffreys, 659, 1355
 Mottsnith Jr., H. M., 1517
Moureu, Charles, 1145-1156; 997-1012
 Müller, Franz von Reichenstein, 298
 Müller, Friedrich von, 1527
 Muir, Alex, 1586; — M. M. Pattison, 1023
Multhauf, Robert P., 47-63; 74-79; 161
 Munitz, Milton K., 1083
 Muntz, Achille, 684
 Muspratt, James, 777, 938; — Sheridan, 938
 mustard gas, 1216, 1290, 1340
 mutarotation, 1168, 1541

 Nagelschmidt, Gustav, 1583
 naphtha, 761, 1114
 naphthalene, 1290
 naphthalene monosulfonic acids, 474
 naphthalenic acids, 1114
 Napoleon I, 317
 Nasini, Raffaello, 671
Nauckhoff, Sigurd, 865-874
 naval stores, 1412
Nef, John Ulric, 1129-1143; 1161
 Neisser, Max, 1055
 neon, 1005, 1456
Nernst, Walther, 1203-1208; 683, 1103, 1291, 1509
 Nesmeyanov, A. N., 1342
 Nestorians, 15
 Neumann, A., 1035
 neurine, 855
 neutrons, 1270, 1358
 Newell, L. C., 479
 Newkirk, William B., 1547
 Newlands, John Alexander Reina, 724
 Newton, Isaac, 137
 Nichols, M. L., 1261
 Nicholson, William, 377, 630

 nickel arsenide, 512
 Nicolaus Kryfts of Cusa, 98
 nicotine, 1558
 niter, 233
 nitric acid, 762; — oxide, 1509
 nitrogen, 232, 1000; — cyanide, 1002; — dioxide, 1444
 nitromethane, 894
 nitrosyl chloride, 840
 nitrous acid, 243, 374, 563
 nitryl fluoride, 970
 Nobel, Alfred, 1287; — Ludwig, 1287; — Robert, 1287
Noelting, Emil, 1013-1018
 nomenclature, 274
 Norman, Walter, 1549
 Norris, James F., 1156
 Nott, Eliphalet, 428
 Noyes, William A., 820, 829
 nucleation, 1518
 nucleic acid, 991, 1321
 nuclein, 1034

 Occlusion of gas, 567
 oceanic salt deposits, 956
 octet theory, 1382, 1512
Odling, William, 551-571; 699, 724, 886
 Oehler, Karl, 635
 Oersted, Hans Christian, 492, 608
Oesper, Ralph E., 601-623
 Ogg, William, 1580
 oil of bitter almonds, 512
 Oldenburg, Henry, 143
 oleic acid, 438
 oleum acidum vitrioli, 123
 olivine, 1578
 Olney, Louis A., 770
 Onsager, Lars, 1501
 opium, 160, 516, 971
 Oppenheim, Alphons, 837
 organic radicals, 1142
 organo-metallic compounds; 890, 1337, 1380
 organotrope, 1049

INDEX

- osmotic pressure, 557, 564, 1103
- Ostwald, Wilhelm, 1019-1030;** 942, 955, 1102, 1435
- Owen, B. B., 1109
- Owens, R. B., 1348
- oxidation of phosphorus, 563
- osido-reduction, 1089, 1255
- oximes, 1071
- oxygen, 247, 374
- oxygenated muriatic acid, 318, 351; — water (hydrogen peroxide), 353
- oxyhydrogen blowtorch, 422
- Ozarovskaya, O. E., 730

- Pachter, Henry M., 62
- Pagel, Walter, 63, 99
- Paine, H. S., 1542
- Palissy, Bernard, 117
- Palladium, 568
- Palmaer, Wilhelm, 1093-1109*
- palmitic acid, 438
- panacea antimonialis, 121
- pancreatine, 461
- Paphnutia, 3
- Papin, Denis, 148
- para-benzoquinone, 1137
- Paracelsus, 47-63;** 286
- Paragranum, 51
- paraldehyde, 533
- paramagnetic substances, 478
- parasitotrope, 1049
- Parravano, Nicolà, 943
- Partington, J. R.; 81-114*
- Pasteur, Louis, 641-660;** 914
- Paternò, Emanuele, 943.
- Patterson, T. S., 79
- Paulze, Jacques Alexis, 266
- Payen, Anselmr, 495-504**
- Péan de Saint-Gilles, 681
- Pebal, Leopold von, 895
- Pechmann, Hans, Freiherr von, 1161
- peptous solutions, 566
- Péligot, Eugène Melchior, 297
- Pelletier, Joseph, 85, 444, 604
- Penington, John, 312
- peptous solutions, 566
- perchromic acid, 964
- periodic system, 723
- Peripatetics, 10
- Perkin, Arthur George, 632, 768
- Perkin, William Henry, 757-772**
- Perkin, William Henry Jr., 1161
- permanganic acid, 490
- pernicious anemia, 1048
- Perrin, Jean, 1498
- Persoz, Jean François, 438
- Peter the Great, 204
- Petit, Alexis Thérèse, 401, 592
- petroleum, 694, 722, 923, 928
- Pettenkofer, Max Joseph von, 538
- Petterson, Otto, 1096
- Petty, William, 139
- Pfeiffer, Paul, 1233-1243*
- phase rule, 796, 1250
- phenanthrene, 1450
- phenol, 1230
- phenylurea, 631
- phellandrene, 841
- phenylacetylene, 1137
- Phillips, Max, 495-504*
- Philosophers and Practitioners, 7-12**
- philosopher's stone, 17
- Philosophical Alchemists and Practical Metallurgists, Thirteenth to Sixteenth Centuries, 39-46**
- philosophical vessel, 44
- phlogisticated air, 232
- phlogiston, 173, 189, 207, 311
- phocenic acid, 439
- phosgene, 1198, 1340
- phosphates, 483, 547
- phosphoric acids, 555, 1292
- phosphorus, 308, 490; — sulfide, 196; — trifluoride, 966
- photography, 1255
- phthalein, 741, 984
- phthalic anhydride, 741
- physical chemistry, 955, 1024

- phytol, 289
 picrotoxin, 444
 Pictet, Amé, 292
Pietsch, Emil, 453-463; 134
 Piloty, Oscar, 989, 1423, 1527
 pinene, 837
 Piria, Raffaele, 665
 Pirogov, N. I., 721
 Pitcairn, Archibald, 103
 pittacal, 636
 Planck, Max, 1206
 plant acids, 257; — ashes, 546
 platinum, 423, 568, 609
 Plato, 10, 21
 Playfair, Lyon, 577, 631, 888
 Plicque, Jules, 961
 Plücker, Julius, 1266
 pneumatic chemistry, 242
 Poggendorff, Johann Christian, 489, 517
 Pohler, apothecary, 256
 Poincaré, Henri, 1266
 polarimeter, 647
 polyamides, 1609
 poly-basic acids, 544
 polymerization, 1089, 1142, 1171
 pondus naturae, 328
 Pope, William Jackson, 1163
 potash, 547, 957
 potassium, 365; — chloride, 196;
 — hydride, 976; — nitrate, 816;
 — soap, 438
 Pott, Johann Heinrich, 295, 639
 Prandtl, Wilhelm, 493
 Precht, Heinrich, 957
Pregl, Fritz, 1325-1331; microanalysis, 1320
 Prescott, Albert Benjamin, 1211
 pressure equipment, 472
Priestley, Joseph, 239-251; 217, 233
 principle of maximum work, 682
 Probierebüchlein, 45
 propionic acid, 889
 propyl alcohol, 680
 protamines, 1035
 protein structure, 132
 proton, 1270
 protoplasm, 286
Proust, Joseph Louis, 325-332; 299, 323
 Prout, William, 379, 524, 591
 prussiate of potash, 198
 Prussic acid, 320, 364
 pseudo-acids, 1079
 psychology of color, 445
 Ptolemy, 21
 pterins, 1448
 pulegone, 845
 purine, 991
 Putnam, Mark E., 1232
 pyridine, 292
 pyrimidine, 991
 pyrochemistry, 862
 pyrogallol, 329
 pyrolusite, 576
 pyrophoric iron, 963
 phosphorus of Homberg, 258
 pyrophosphoric acid, 562
 pyrrole, 1530
 Quantum theory, 1306, 1499
 quicklime, 214
 quicksilver, 329
 quinine, 290, 760
 quinone, 516, 1446
 Rabies, 656
 radicals, 711
 radioactivity, 1267
 radium family, 1350
 Radot, René Vallery, 659
Ramsay, William, 997-1012; 225, 1465
 Ramser, Hans, 1430
 Ranc, Albert, 685
 Ranelagh, Lady, 138
 Raoult, Francois Marie, 1010
 Rappaport, Rhoda, 192
 rare earths, 942
 Ravenna, Ciro, 1090

- Rayleigh, Lord, 1000, 1346
 Raymond, Albert L., 1322
 Raymundus Lullus, 41
 reaction mechanism, 679
 receptor, 1053
 Reddelien, Gustav, 1075
 Redman, John, 1183; — L. V., 1419
 Redtenbacher, Joseph, 1152
 Reformatskiĭ, S. N., 694
 Regaud, Claude, 1272
 Regnault, Henri Victor, 752
 Regis, Pierre Sylvain, 160
 Reichenbach, Carl, 636
 Reimann, Karl Ludwig, 768
 Reinmuth, Otto, 1342
Remsen, Ira, 819–822; 770, 817, 1131
 Renan, Ernest, 677
 reversibility, 792
 Reynolds, Emerson, 1162
 Rhazes, 25
 rhubarb, 258
 ribose, 1321
Richards, Theodore William, 822–826; 524
 Richtmeyer, N. K., 1549
 Riesenfeld, Emil, 1109
 Rimsky-Korsakov, 1316
 Rive, Auguste de la, 391
 Roberts, W. Chandler, 568
 Robinson, Elihu, 335
 Robinson, Robert, 1156
 Robiquet, Pierre-Jean, 444, 516
 Rockefeller, Frank; 928; — John D., 1134
 Röntgen, Wilhelm Conrad, 985, 1073, 1115, 1265
 Rohault, Jacques, 160
 Rohdewald, Margarete, 1372
 Rollett, Alexander, 1330
 Roozeboom, Bakhuis, 751, 790, 1250
 rosaniline, 636, 764
Rosbaud, Paul, 1563–1586
 Roscoe, Henry Ernest, 578, 1160
 Rose, Friedrich, 984; — *Gustav*, 481–493; 509; — Heinrich, 392, 485, 509; — Valentin, 295
 Rossbach, Michael G., 1062
 Roth, Hermann, 1328
Rouelle, Guillaume-François, 185–192; 265
 Rouelle, Hilaire-Marin, 188
 Rousseau, Jean-Jacques, 188
 Rowland, Henry A., 785
 rubidium, 579
 rubrene, 1155
 Ruckeyser, Muriel, 801
 Rühle von Calw, Ulrich, 43
 Rumford, Count (Benjamin Thompson), 375
 Runge, Frielieb Ferdinand, 632, 939
Rush, Benjamin, 303–314
 Ruska, Julius, 29, 37, 599
 Ruskin, John, 878
 Russell, Harry L., 810
Russell, Alexander S., 1463–1468
 Rutherford, Daniel, 217
Rutherford, Ernest, 1343–1363; 289, 1008, 1269, 1381
Ruzicka, Leopold, 831–851
 Sabatier, Paul, 685, 1285, 1339
 saccharinic acid, 258, 1141
 safety lamp (Davy), 380
 sal ammoniac, 32, 90; — enixum, 120; — mirabile, 120
 salsum, 104; — tartari, 132; — vegetabile, 41
 salicylic acid, 707, 816, 894
 saltpeter, 104, 308
 salts, 28
 salvarsan, 1061, 1198
 Sandmeyer, Traugott, 858
 saponification, 440
 sarcosine, 894
 Sarton, George, 9, 451
 Saussure, Horace-B. de, 189, 391
 scandium, 724
 Sceptical Chymist, 141

- Schaefer, Vincent J., 1576
Scheele, Carl Wilhelm, 253–261;
 195, 218, 231, 608
 Scheele's green, 257
 Scheibler, Carl, 634
 Scherer, Edmond, 189
 Schering, Ernst Friedrich Christian, 634
 Schimank, Hans, 366
 Schlenk, Wilhelm, 1213, 1445, 1554
 Schlesinger, Hermann Irving, 1429
 Schloesing, J. J. Théophile, 684, 777
 Schmitt, Rudolf, 894
 Schmorl, Karl, 746
 Schönbein, Christian Friedrich, 319
 Schöpf, Clemens, 1448
Schoepfle, Charles Seitz, 1209–1217
 Schorlemmer, Carl, 1160
 Schrader, Hans, 1437
 Schröder, Heinrich Georg Friedrich, 597
 Schützenberger, Paul, 969
 Schumacher, Johann Daniel, 205
 Schuster, Arthur, 1352
 Schwann, Theodor S., 650
Scientists and Industrialists, 935–945
 scorbutic, 332
 Searles Lake brines, 1416
 sea water, 1492
Secrétan, Claude, 185–192
 sedoheptose, 1543
 Sefström, Nils G., 392
 Seguin, Armand, 276
 selenium, 289, 490, 518
 Sementsov, A. J., 696
 Semet, Florimond, 775
 Semmelweiss, Ignatz, 655
 Semmler, F. Wilhelm, 844
 Senac, 169
 Senderens, Jean Baptiste, 1285
 sensitizers, 1259
 sesquiterpenes, 842
 Sertürner, Friedrich Wilhelm, 444
 Seybert, Henry, 407
 Shaw, Peter, 169
 Sheffield, Joseph E., 415
 shellac, 1187
 Shields, John, 1000
 Shiga, Kioshi, 1055
 Shippen, William, 309
 side-chain theory, 1053
 siderophile, 1569
Sidgwick, Nevil Vincent, 1375–1387;
 291, 943
 Siecke, Wolfhart, 1428
Siegfried, Robert, 369–384
 Siemens, Werner von, 974
 silica, 257, 913, 1371
 silicate rocks, 390
 silicon, 575, 611; — carbide, 1424;
 — hydrides, 1427; — organic
 derivatives, 1170; — tetrachlo-
 ride, 1171
 silkworm, 652
Silliman, Benjamin, 403–417
 Silver, Paolo, 1089
Silverman, Alexander, 907–920
 Sisco, Annaliese Grünholdt, 46
 Scaup, Zdenko, 1330
 van Slyke, D. D., 1324
 Smith, Alexander, 1135, 1143
 Smith, Angus, 559
Smith, Edgar Fahs, 826–830; 251
 Smith, T. A., 1174
 Smithsonian Institution, 429
 Sobrero, Ascanio, 392
 Société d'Arcueil, 363
Soddy, Frederick, 1008, 1349;
1463–1468
 Soderbaum, Henrik Gustav, 402
 sodium bicarbonate, 779; — ions,
 1101; — soap, 438
 solidification, 477
 solubility, 592
Solvay, Ernest, 773–782; 942
 Sørensen, Søren Peter Lauritz, 1494
 sorghum, 814

INDEX

Southey, Robert, 375
 Soxhlet, Franz, 809
Späth, Ernst, 1551-1562
 Spanish white, 152
 sparteine, 1151
 specific heat, 220; — volume, 595
 spectrum, 579
 Speter, Max, 599
 spices, 22
 Spiess, G., 509
 Spinoza, Baruch, 167
 spiritualism, 432
 spiritus ardens, 126; — arsenic ni-
 tros, 125; — nitri, 124; — salis,
 125; — urinae, 101; — vini, 126
 Spitalski, E. I., 1292
 Spoehr, Herman A., 1135, 1142
 Squires, F. B., 928
 Stähler, Arthur, 1425
 Stahl, Georg Ernst, 170, 296, 328
 stannic acids, 1176
 Stapleton, H. E., 17, 36
 Stas, Jeans Servais, 525, 700, 1124
 stearic acid, 438
 steel, 798
 Steenbock, Harry, 811
 Stenhouse, John, 630
 stereochemistry, 647, 861, 1071,
 1237
 Steudel, Hermann, 1035
 Stevenson, Earl P., 1201
 Stieglitz, Julius, 1134
Stock, Alfred, 1421-1432; 959-979;
 942
 Stokes, Gabriel, 891
 strength of acids, 1080
 Stromeyer, Friedrich, 455, 513
 strontia, 298
 strontium, 379
 structural formulas, 707
 strychnine, 129
 Stubbe, Henry, 143
 sublimation apparatus, 24
 substitution theory, 531, 628
 sugar cane, 198

sulfates, 484
 sulfite pulping process, 1195
 sulfonic acids, 868
 sulfur, 19, 146, 1476; — fluoride,
 970
 sulfuric acid, 243, 365
 sulfur mining, 924
 surface films, 1515
 Svedberg, Theodor, 992
 Swartz, Edward, 1183
 Sweetser, Samuel P., 1520
 sylvestrene, 841
 synoptic formulas, 885
 synthesis, 527, 679; of mannose,
 990
 synthetic fibre, 1610
 system of colors, 1028

 Table of atomic weights, 401
 Tachenius, Otto, 107, 145
 Tafel, Julius, 989
 Takamine, J., 770
 talloil, 1116
 Tammann, Gustav, 1539
 Tapputi-Belatekallim, 1, 3
 Tartarus, 196, 286
 tartaric acid, 295, 646
 Taubert, I. K., 209
 Tauler, Johann, 83
 taurine, 461
 tautomerism, 1074, 1132
 Taylor, Alonzo E., 817
 Taylor, F. Sherwood, 36
 Taylor, H. S., 1483
Teeple, John Edgar, 1409-1420
 tellurium, 289, 299
 Temkin, Owsei, 62
 Tennant, E. W. D., 944
 terephthalic acid, 837
 terpenes, 745, 836, 841
 tetraethyl lead, 1231, 1589
 tetrahydronaphthalene, 1290
 tetraiodopyrrol, 1088
 tetraphenylhydrazine, 1214, 1444
 Thales of Miletos, 9

- thallin, 1051
 Thelen, Tobias R., 1096
The Chemists' Language, 283-292
Thenard, Louis Jacques, 343-357;
 604, 1447
 Theophrastus of Eresos, 11
 Theosebia, 3
 theriac of Andromachus, 156
 thermionic emission, 1513
 thermochemistry, 679
 thermodynamics, 792, 794, 911,
 1206, 1473
 thermoscope, 100
 Thiele, Johannes, 1143, 1443
 thiophen, 858
 third law of thermodynamics, 1208
 Thomas a Kempis, 83
 Thompson, Benjamin, 785
 Thomsen, Julius, 1022, 1485, 1495
Thomson, George Paget, 1453-1462
 Thomson, James, 793, 1346
 Thomson, J. J., 1456
 Thomson, Thomas, 171, 395, 408
 Thomson, William, 791
 thorium, 390, 1348, 1513
 Thorndike, Lynn, 46
Thorpe, Thomas Edward, 583-599;
 1162
 Thudichum, Ludwig, 549
 thujone, 849
 thymus, 1035
 Tiedemann, Fritz, 460, 509
 Tiemann, Ferdinand, 744
Tiffeneau, Marc, 1389-1396
 Tilden, William A., 338, 480, 732,
 838
 Tillet, Mathieu, 278
 Tilley, C. E., 1586
 tin, 34, 73
 tinctura silicum, 131
 Tipson, Stuart R., 1324
 Tissandier, Gaston, 448
 titanium, 298
Tizard, Henry Thomas, 1375-1387
 toluidine, 631
 Tonks, Lewi, 1517
 Toricelli, Evangelista, 556
 Townsend, J. S., 1346
 Traube, Ludwig, 655, 1042; —
 Moritz, 1446
 Travers, Morris William, 1004
 Trevor, Joseph E., 1251
 trimethylrosaniline, 632
 triphenylmethyl, 1212
 Trithemius, Johann, 41
 Trommsdorf, Christian Wilhelm,
 457
 Troost, Louis, 615
 Tropsch, Hans, 1438
 trypan red, 1059
 Tschirnhaus, Ehrenfried Walter von,
 153
 Tswett, Michael, 1371
 tuberculin, 643, 1052, 1318
 Tukulti-Ninurti I, 1, 3
 tungsten, 1510
 tungstone, 257
 turpentine oil, 837
 Tyndall, John, 480, 813
 type theory, 711
 tyrocinium chymicum, 68
 Uhlenhut, Paul, 1059
 Ulstad, Philip, 79
 ultramarine blue, 348
 unitary formulas, 884
 Unmack, Augusta, 1503
 Unverdorben, Otto, 628
 Upson, Fred W., 1142
 uranium, 289, 298, 1266
Urbain, Georges, 521-533; 1339
 Urdang, George, 260
 urea, 511, 530
 urethane, 527
 Urey, Harold Clayton, 1109, 1459
 uric acid, 681, 741
 Valency, 531, 1239
 Valentine, Basil, 60, 97
 Valeur, Armand Charles, 1151

INDEX

- vanadium, 518
- Vauquelin, Louis Nicolas, 298, 346, 940, 964
- Velox paper, 1186
- Venel, G. -F., 188
- verdigris, 130
- Veselovskii, K. S., 727
- Vicq-D'Azyr, Felix*, 177-183
- Vieille, Paul, 684
- Villiger, Victor, 1079
- Vinci, Leonardo da, 668
- Virchow, Rudolf, 651, 1048
- Virtanen, Artturi J., 1116
- vitamin A, 1139
- vitriol, 28, 144, 285
- vitriolated tartar, 181
- Volhard, Jacob, 1137
- Volta, Alessandro, 236, 507
- volume chemistry, 1023
- Voskressenskii, A. A., 720
- Waage, Peter, 681, 796
- van der Waals, Johannes Diderik**, 749-755; 790, 1123
- Waele, Henry de, 114
- Wagner, Gustav, 745, 844
- Walden, Paul*, 115-134
- Waldschmidt-Leitz, Ernst, 1371
- Walker, William H., 1196
- Wallach, Otto**, 831-851
- Wanklyn, James Alfred, 1336
- Warburg, Otto, 1449
- Warren de la Rue, 699
- Wassermann, August von, 1057
- water composition, 97, 190
- waterproofed papers, 1197
- Weeks, Mary Elvira*, 435-451
- Wegscheider, Rudolf, F. W., 1556
- Weigert, Otto, 1054
- weight of the air, 142
- Weinberg, Arthur von, 1048, 1062
- Weissberger, Arnold*, 1065-1083
- Weltzien, Carl, 899
- Wenzel, Carl Friedrich, 321
- Werner, Alfred**, 1233-1243; 1071, 1382, 1493
- Wheatstone's bridge, 1205
- Wheeler, T. S., 715, 801
- Whewell, William, 286, 950
- Whitney, Josiah Dwight, 430
- Whitney, W. R., 1510
- Wiberg, Egon*, 1421-1432
- Wichelhaus, Hans, 634, 834
- Wiedemann, Gustav, 1068
- Wiegand, Johann Friedrich, 298
- Wieland, Heinrich**, 1441-1451; 1525-1533; 746, 1214
- Wieland, Theodor, 1448
- Wiley, Harvey Washington**, 813-819; 770, 1542
- Wilhelmy, Ludwig, 681
- Wilke, Wilhelm, 1402
- Will, Heinrich, 589, 629
- Willard, H. H., 824
- Williamson, Alexander Williams, 699, 886, 1099
- Willstätter, Richard**, 1365-1374; 733-747; 291, 994, 1132, 1310
- Wilson, George, 238
- Wilson, James, 818
- Wilson, Woodrow, 770
- Windaus, Adolf, 1447
- Winderlich, Rudolf, 402
- Wislicenus, Johannes, 952, 989, 1026, 1068, 1114
- Witt, Otto Nikolaus**, 1013-1018; 769, 941, 1046
- Witte, Count Sergius, 729
- Wöhler, Friedrich**, 505-520; 290, 538, 681, 827, 1616
- Wolff, Christian, 204
- Wolff, Emil von, 810
- Wolfson, Melville L.*, 1129-1143; 1313-1324; 1535-1550
- Woll, Fritz, 809
- Wollaston, William H., 488
- Wood, Francis Carter*, 1263-1275
- wood chemistry, 127, 871, 1412
- wood wastes, 1197

- Woodhouse, James, 406, 422
Woskresensky, Alexander, 516
Wren, Christopher, 139
Wurtz, Charles-Adolphe, 521-533;
290, 709, 1139

Xenon, 1005

Yahya ibn Khalid, 18
yeast, 1034
Yoffe, S. T., 1342

Young, S., 999
Yttrium, 390

Zaitsev, Alexander, 694
Zeise, William Christopher, 868
Zelinsky, Nicolai Dimitrejewitsch,
1114
zinc, 131, 198; — ethyl, 1592
Zincke, Theodor, 1527
Zinin, Nikolai Nikolaevich, 689,
1316, 1324
Zosimos, 3, 11

This edition consists of 300 copies,
numbered 1 through 300.

The composition has been done by
Westcott and Thomson of Philadelphia
in Linotype Fairfield medium,
designed in 1941 by Rudolph Ruzicka
for the Mergenthaler Linotype Company;
and the printing was executed by
New York Lithographing Corporation of New York City.

Paper for this edition was specially made by
The Mohawk Paper Mills, Inc., of Cohoes, New York.

The book was designed by Ernst Reichl.
The binding was done by J. F. Tapley Company,
Long Island City, New York.

This is Copy number: 166

